

## 8. VAPOUR PRESSURE

It is known that adding ethanol to gasoline raises the vapour pressure of the fuel. The chemical explanation for this is that gasoline consists mainly of hydrocarbons (straight, branched and aromatic hydrocarbons), which are nonpolar and have different boiling points. In contrast, the ethanol molecule ( $\text{CH}_3\text{CH}_2\text{-OH}$ ) contains a hydroxyl group ( $-\text{OH}$ ) which makes it polar. It is a well-known fact from solubility investigations that like dissolves like, i.e. polar solvents dissolve polar solutes and nonpolar solvents dissolve nonpolar solutes. Thus, introducing polar compounds like ethanol into gasoline (which is nonpolar) makes the gasoline blend more polar than neat gasoline, and increasingly polar as the ethanol content increases. This results in the vapour pressure of the ethanol-gasoline blend rising, since nonpolar compounds in the neat gasoline, with relatively low boiling points (and hence relatively high vapour pressure), will evaporate as the gasoline blend becomes more polar. In Figure 8.1 the Reid Vapour Pressure (RVP) (measured, by definition, at 100 °F) is shown as a function of the percentage of ethanol blended with gasoline. The neat gasoline from 1997 (Furey and Jackson, 1977) had a higher initial vapour pressure than the gasoline from 2002 (Hsieh et al., 2002). The lightest chemical component of gasoline fuel in general is butane, which is removed to produce low RVP gasoline (Korotney, 1996). This indicates that the evaporative emissions from ethanol blended gasoline consist mainly of butane.

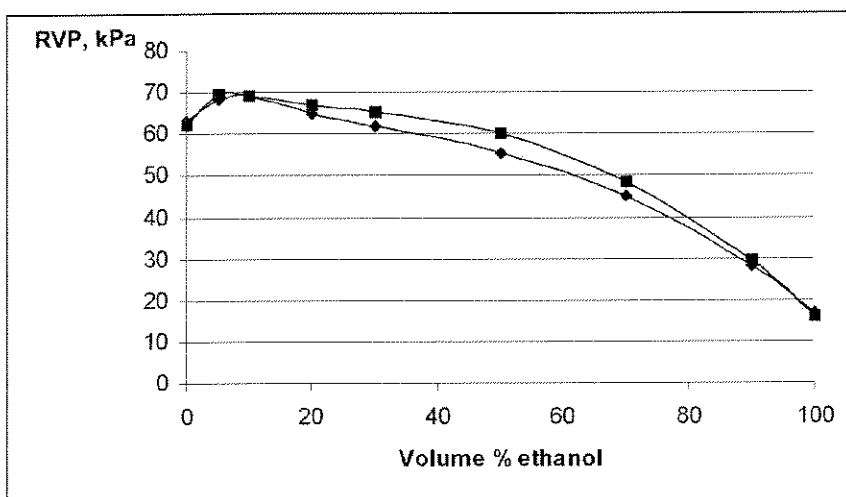


Figure 8.1. Reid Vapour Pressure (at ~38 °C) shown as a function of the percentage of ethanol blended with gasoline (■ Furey and Jackson, 1977; ◆ DOE, 1991).

For both of the fuels shown in the figure the highest relative RVP was obtained at a percentage of ethanol in the neat gasoline of about 10%. Hence, there are strong indications that the maximum RVP will be obtained at a 5 to 10 percent ethanol content in gasoline, regardless of the neat gasoline fuels used. Decreasing the initial vapour pressure of the neat gasoline will reduce the absolute vapour pressure of a 10 percent ethanol blend. Furthermore, in Figure 8.1 the largest vapour pressure increase (a approximately 10 % increase in the RVP) is observed in the 0 to 5 percent ethanol interval. A compound in gasoline which has a major impact on the RVP is butane (Korotney, 1996).

The compounds in the vapour phase from regular, mid and premium grade gasoline containing ethanol (3.25 to 9.65 wt%) have been investigated by Harley and Coulter-Burke (2000), in a headspace analysis in which they concluded that n-butane, n-pentane, 2-methylbutane and ethanol collectively accounted for more than 50% of the total headspace vapour mass at 38 °C.

A large number of paper and reports have focused on the fact that blending ethanol in gasoline increases the vapour pressure, and this phenomenon has been investigated in a number of studies, especially in the USA, for example “Issues Associated with the Use of Higher Ethanol blends” (NREL 2002). In the early 1980s Furey (GM) reported that even a low level of alcohol in gasoline could have a high impact on the vapour pressure of the fuel (Furey 1985; 1986; 1990). A commonly quoted figure for the increase in RVP when blending base gasoline available on the US market with 10% ethanol is 1 psi (a little less than 7 kPa), see below concerning the “1 psi waiver”.

A report prepared for the Swedish Transport and Communications Research Board presented a limited investigation of two fuels (one vapour pressure-adjusted and the other unadjusted) used in three cars (see also section 7.4). The increases in vapour pressure found after adding 10 % ethanol were 5 kPa and 4.5 kPa, respectively.

In many countries, including European countries, RVP is commonly expressed in kPa units, while psi (pound per square inch) is used in the USA. To facilitate comparisons, a graph for converting psi to kPa and vice versa (based on a psi to kPa conversion factor of 6.895) and psi to  $\text{kp}/\text{cm}^2$  (another unit for measuring RVP used in some reports) is shown in Figure 8.2.

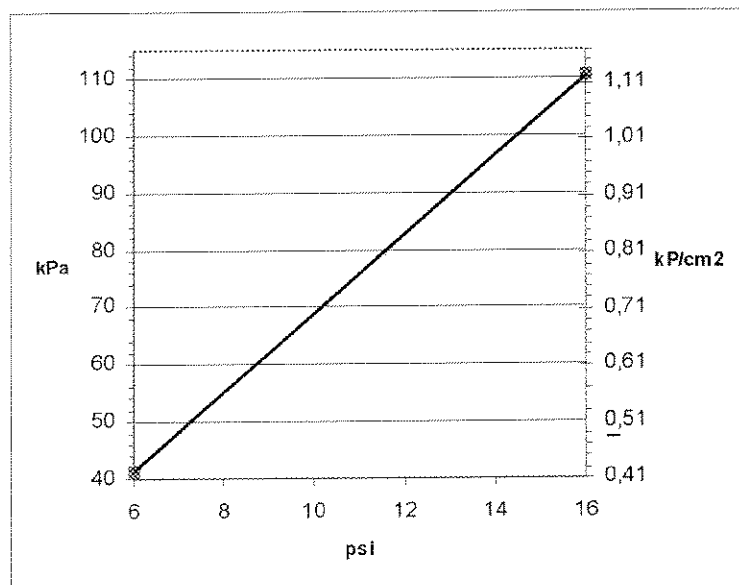


Figure 8.2. Graph for converting psi to kPa and  $\text{kp}/\text{cm}^2$ .

An important issue in several countries related to the increase in vapour pressure caused by mixing gasoline with ethanol has been whether or not compensatory adjustments should be made to the vapour pressure of the base gasoline. If it is not adjusted the RVP may increase above regulated limits and may result in increased evaporative losses. Since many countries have regulations concerning RVP failing to meet the standards may even be illegal. In the EU, the RVP of gasoline is regulated by the European gasoline standard (EN 228).

Since a high vapour pressure of the fuel may cause vehicle drivability problems and make hot starting impossible as a result of vapour lock, another relevant issue is driver acceptance of the fuel.

According to the literature some countries at least, such as the USA, Australia and Sweden, have decided to decrease the vapour pressure of the base gasoline used in alcohol blends in order to meet the existing standards/regulations.

### **8.1. RVP - USA**

In the USA the vapour pressure of 10% ethanol-gasoline blends has been allowed to exceed the limits imposed for conventional gasoline by 1 psi (the "1 psi waiver" Andress, 2000).

There has been ongoing debate in the USA about whether or not this waiver should be retained. The US EPA has been arguing that the waiver for ethanol-blended gasoline can be seen as a barrier hindering the broader introduction of reformulated gasoline. On the other hand, there has been pressure from the farmers producing ethanol and the Ethanol Fuel Association, since an increase in the use of ethanol, as a replacement for MTBE, would increase demand for ethanol. One factor to take into account, especially for the US EPA, is that the use of ethanol blended gasoline is recommended in CO non-attainment areas.

Documents from the California Air Resources Board (CARB) (CARB, 1998) show that replacing gasoline with ethanol may clearly reduce CO emissions, even if the gasoline is not adjusted to comply with RVP requirements (i.e. the 1 psi waiver is applied). Thus, adding ethanol to gasoline has provided a means to meet CO levels required by the air quality standards in many of the current, so-called CO non-attainment areas. However, these documents also show that adding ethanol to gasoline without adjusting the RVP leads to increases in the emissions of volatile organic compounds (VOCs) and nitrogen oxides (NO<sub>x</sub>), and in the fuel's ozone-forming potential. Since both VOC and NO<sub>x</sub> are important emissions in the formation of tropospheric ozone the 1psi waiver has not been applied to mixtures of ethanol in reformulated gasoline (RFG), which is primarily intended for use in ozone non-attainment areas to avoid increased formation of ozone.

The effect of this waiver is discussed in a study released by the EPA that provided part of the rationale for introducing reformulated gasoline (RFG), i.e. gasoline containing an oxygenate, which at the time could be either MTBE or ethanol (US EPA, 1993). It was proposed that a renewable oxygenate should be used, and one of the most controversial questions addressed when the RFG rule was drafted was how ethanol/gasoline blends should be treated. The EPA argued that the base gasoline had to be adjusted to ensure that the vapour pressure met the standards. However, the EPA had to accept that adjusting the RVP could lead to cost penalties, *inter alia*, for the ethanol blended fuel. An argument propounded in comments sent to the EPA was that ethanol would be excluded from the market without a waiver. The opinion among the rule makers within the EPA was that ethanol is cheaper than MTBE per gallon and that this cost difference could well compensate for the costs of adjusting the RVP, which are minor compared to the cost of adding oxygen via oxygenate additions.

In the cited paper (US EPA, 1993) the EPA also discussed the detrimental effect on emissions of granting the waiver of 1 psi RVP, since blending ethanol in gasoline will increase the vapour pressure of the fuel, and hence increase VOC emissions. Two letters from EPA staff claim that a fuel that met RFG requirements in every respect except its RVP and had an RVP of 1 psi over the limit would increase VOC emissions by about 20 % relative to a baseline gasoline.

Furthermore, the EPA argued at that time that ethanol blends with a 1 psi waiver would have an advantage over RFG and thus might dominate the market (US EPA, 1993).

The estimated reduction in VOC emissions likely to follow the introduction of RFG based on unblended gasoline is estimated to be 11 %, see Table 8.1. The reduction will be less if ethanol blended gasoline is used, and considerably less if RVP-adjusted gasoline is not used as a base according to the EPA estimations. Consequently, the reduction in VOC emissions will diminish as the ethanol market share increases, as can be seen in Table 8.1.

Table 8.1. Losses of "In-Use" VOC Emission Control as a Result of the Ethanol Waiver for RFG\*

	Ethanol Market Share (%)				
	0	8	24	30	35
% VOC Reduction Due to MTBE Share	11	10.1	8.4	7.7	7.2
% VOC Reduction Due to Ethanol Share (with distillation)	0	-1.0	-3.1	-3.9	-4.6
% VOC Due to Commingling	0	-1.2**	-2.4	-2.4	-2.4
Total % VOC Reduction	11	7.9	2.9	1.4	0.2
Percentage Change from 100% MTBE Baseline	N/A	28	74	87	98

\* Emission percentage change input values shown are based on those calculated in the letter from Chester France to Dr. Gary Whitten. Memorandum 6 from Paul A. Machiele, Fuel Studies and Standards Branch, to Richard D. Wilson, Director, Office of Mobile Sources, "Update of the Relative Ozone Reactivity of Reformulated Gasoline Blends," June 11, 1993.

\*\* Commingling, assuming half of that at higher market shares based on analysis (US EPA, 1993).

A paper from the US Energy Information Administration section (EIA, 2002) of the US Department of Energy (DOE) describes, *inter alia*, the effect of adjusting the RVP of base gasoline intended for blending with ethanol. A primary feature it displays is that there is a relationship between the RVP of the base gasoline, and the magnitude of the impact on the RVP when adding ethanol to the base gasoline is shown in Table 8.2

Table 8.2. RVP effect of blending ethanol to the base gasoline.

Finished Gasoline RVP Requirement	Approximate RVP Increase when Ethanol is Added to Make a 10% Blend	Base Gasoline RVP Adjustment Needed if 1 Pound Waiver Not Allowed
9.0	1.0	(1.1)
7.8	1.2	(1.3)
7.0	1.3	(1.4)

Sources: William J. Piel, "Oxygenate Flexibility for Future Fuels," Acro Chemical Company, paper presented at the National Conference on Reformulated Gasoline and Clean Air Act Implementation, Information Resources, Inc. Washington, DC, October 1991, American Petroleum Institute, *Alcohols and Ethers*, Publication 4261

The paper cited above (EIA, 2002) discusses the energy losses from the gasoline pool due to removing C<sub>4</sub> and C<sub>5</sub> hydrocarbons from it in order to meet the RVP requirements of gasoline without the 1-psi waiver. The study that the paper was based upon was initiated by discussions about the possible removal of the 1-psi waiver following a request by Senator Bingaman

(Chairman of the Senate Committee on Energy and National Resources) presented in a separate paper (Office of Oil and Gas of the Energy Information, 2002).

It is interesting to note that an adjustment of the base gasoline intended for use with ethanol blends in order to keep the RVP under the required limits may reduce the energy content of the gasoline pool to a larger degree than the energy supplied by the added ethanol (EIA, Energy Information Administration, 2002). However, the magnitude of the reduction in energy content depends on the RVP requirement and the gasoline used for blending. In the USA, especially California, where the maximum RVP allowed is 7.0 psi (48.3 kPa), adjustment of the gasoline to be used for blending with 10 % ethanol will result in a 2.8 % reduction in its energy content. In contrast, in areas of the USA where the maximum RVP is 9 psi (62.1 kPa) the result of adding 10 % ethanol to RVP adjusted gasoline will be a 4.5 % increase in the energy content. Not adjusting the base gasoline intended for use in 10 % ethanol blends will result in a 5.1 % increase in the energy of the gasoline pool if there is a 7.0 psi RVP requirement and a 7.5 % increase if there is a psi 9.0 RVP requirement.

These two examples could be used as models for calculating the effect of adjusting the base gasoline for blending, in energy terms, when deciding whether it should be adjusted or not. However, it should be emphasised that the components (mostly butane) removed from the base gasoline when adjusting the RVP will generally be used for other purposes and not wasted. The increase in evaporated hydrocarbon emissions that will occur if the RVP is not adjusted should be analyzed and discussed when deciding whether these polluting emissions will be unacceptably high (see table below).

<b>Volume and Energy Effects of Adjusting RVP Prior to Adding Ethanol</b>				
<b>RVP</b>	<b>Volume Change due to Adding Ethanol to Make a 10% Ethanol Blend</b>		<b>Energy Change due to Adding Ethanol to Make a 10% Ethanol Blend</b>	
	<b>With RVP Waiver</b>	<b>Without RVP Waiver</b>	<b>With RVP Waiver</b>	<b>Without RVP Waiver</b>
9.0	11.1%	7.5%	7.5%	4.5%
7.8	10.3%	2.2%	6.8%	-0.2%
7.0	8.3%	-0.9%	5.1%	-2.8%

A paper published by the US EPA (Korotney, 1996) considers RVP-related characteristics associated with three different gasoline blends: "Low RVP gasoline", "Reformulated gasoline (RFG)" and "Conventional gasoline". Low RVP gasoline is produced from conventional gasoline by removing butane (EPA 1996), while RFG is "blended to burn cleaner and reduce smog-forming and toxic pollutants" (Virginia Department of Environmental Quality 2005). Conventional gasoline is a mixture of compounds, called hydrocarbons, refined from crude petroleum, plus small amounts of a few additives (Utah Petroleum Association, 2004). Conventional gasoline is also called "Commercial gasoline" and in certain areas of the USA will be blended with ethanol (commonly to 10 %).

Korotney addresses implications of the facts that the only compound removed from conventional gasoline is butane and that low RVP gasoline is produced solely to meet the RVP requirements of 6.8 psi to 8.1 psi, with typical values of 7.0 to 7.2 psi. Since the intentions when designing reformulated gasoline were not only to meet the RVP requirements, but also to reduce emissions

of toxic substances, his conclusions concerning low RVP gasoline, compared with conventional gasoline are *inter alia* that:

- Low RVP gasoline will reduce the evaporative emissions.
- The primary emission benefits (VOC) of low RVP gasoline come from reductions in evaporative emissions.
- Exhaust emission reduction is very small or nonexistent.
- Low RVP gasoline will have little or no effect on NO<sub>x</sub>.
- Evaporative emissions of VOC tend to be less reactive (i.e. produce less ozone) per gram than exhaust VOC.
- Since nitrogen oxides (NO<sub>x</sub>) are combustion products, they will not be found in evaporative emissions, so using low RVP gasoline should have little or no effect on NO<sub>x</sub> emissions. However, empirical evidence indicates that use of low RVP gasoline may actually increase the NO<sub>x</sub> emissions by 1 %.
- Low RVP gasoline will not reduce carbon monoxide (CO) emissions, and may in fact increase them slightly. RFG gasoline, on the other hand, will affect CO emissions since they are influenced by the oxygen content of the fuel and not the RVP.
- Since ozone is formed in the atmosphere from complex reactions involving NO<sub>x</sub>, VOC and CO, reducing the RVP will have less effect on its levels than using RFG, which will have also affect NO<sub>x</sub> and CO emissions.

Another paper released by the EPA (US EPA, 1996) represents a response to a letter from the American Petroleum Institute (API) is presented (US EPA, 1996). The director of the API, C.J. Krambuhl, opposed statements of the EPA (Korotney) in their paper about low RVP gasoline. The main argument by Krambuhl was that the low RVP gasoline is more cost-effective than the reformulated gasoline. In a short answer to the API, the EPA's Fuels and Energy Division Director, C.N. Freed, notes that "The modest reductions in NO<sub>x</sub> for Phase I, RFG, and the more substantial reductions in NO<sub>x</sub> for Phase II, RFG, provide a means for immediately reducing ozone without waiting for fleet turnover". He also invited the API to a meeting with the EPA in order to clarify the latter's position. In a report (US EPA, 1999) it is stated that "Beginning on January 1, 2000, the Phase II complex model standards at 40 CFR 80.41(e) and (f) will apply to all RFG in the gasoline distribution system".

## 8.2. RVP - Brazil

Brazil introduced ethanol as a neat fuel for spark ignition engines more than 20 years ago. The Brazilians have also tried blending ethanol to different levels with gasoline since then. The introduction of ethanol was due more to rural and agricultural politics than to environmental concerns. Hence, the number of relevant emissions tests etc. they carried out was limited. The use of ethanol as a vehicle fuel in Brazil has varied over the years, mainly because of variations in the production capacity and changes in the taxation system. Today, a number of FFVs and vehicles optimised for running on neat ethanol are being used in Brazil. In addition, all marketed gasoline is blended with approximately 20 % ethanol. Furthermore, there is no tax reduction for ethanol in Brazil today, because its low production costs (reduced incrementally over the past 20 years) allow it to compete on the fuel market without any such advantages.

Nevertheless, very few tests have been done in Brazil regarding the environmental effects of using ethanol as a vehicle fuel. Ethanol is regarded as an environmentally friendly fuel with low CO<sub>2</sub> emissions, and no need for further debate is recognised. The potential problems associated with increased vapour pressure due to adding ethanol to gasoline, including increased

evaporative losses, do not apply in Brazil since they use either neat ethanol (with very low RVP) or at least 20 % ethanol blended in gasoline; a level at which the increased vapour pressure has declined more or less back to the original RVP of the base gasoline (Alfred Szwarc, personal communication, 2004).

### 8.3. *RVP - Europe*

In Europe the vapour pressure of gasoline is restricted to:

- A minimum of 45 kPa and a maximum of 60 kPa in summertime.
- In countries with Arctic and sub-Arctic climates, such as Sweden, the RVP must be at least 45 kPa and no more than 70 kPa in summertime<sup>\*</sup>.

In Sweden not many investigations have been carried out on the relationship between ethanol blends in gasoline, increased vapour pressure and increased evaporative emissions. However, one such study is described in the report, mentioned earlier, prepared for the Swedish Transport and Communications Research Board (KFB) by Laveskog and Egeback (1998; see section 7.4).

In another, the vapour pressure and evaporative emissions from E85 (85 % ethanol and 15 % gasoline), E10 and reference gasoline were studied in a project carried out by Lu-Karlsson (1999) at the MTC (Motortestcenter of Sweden). Using a simulated Sealed Housing for Evaporative Determination (SHED) test method, the total amounts of hydrocarbons (HC) that evaporated were quantified and the composition of the evaporative emissions was chemically characterized. The evaporative emission components detected were ethanol, benzene, toluene, C<sub>4</sub>-C<sub>6</sub>, alkanes and olefins. The E10 mixture gave the highest HC evaporative emissions. Compared to gasoline, the E10 gave elevated C<sub>4</sub> – C<sub>6</sub> alkanes and olefin emissions, but reduced aromatic emissions. Compared to the reference gasoline, the base gasoline with a higher vapour pressure gave significantly higher C<sub>4</sub> – C<sub>6</sub> alkane and alkene emissions.

At the European level (ICR – ISPRA), in 2004 Eucar and Concawe carried out a joint investigation of evaporative losses and other phenomena associated with blending ethanol in gasoline. The objectives of the project were:

- To clarify the effect of fuel vapour pressure on volatility and evaporative emissions from modern cars equipped with canisters, representative of the recent European fleet.
- To assess the effect of ethanol blending on fuel properties and evaporative emissions (quantitative and qualitative).
- To assess the impact of the cars' fuel system technology on the evaporative emissions (canister aging, metal/plastic tanks).
- To provide a firm technical basis for debates on gasoline vapour pressure limits in relation to ethanol blending for the Fuels Directive Review.

The tests were to be carried out on two base gasolines (one vapour pressure-adjusted and one unadjusted), and ethanol blends (with 5 and 10 % ethanol contents) of these fuels were to be examined. However, no official report from the project has been presented as yet.

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<sup>\*</sup> During wintertime in Finland, Norway and Sweden the RVP ranges from 50 to 95 kPa.

#### 8.4. RVP - Australia

According to the literature studied there is a clear preference for mixing ethanol in gasoline in Australia. The main issue addressed by the authors involved has been the percentage of ethanol that should be allowed to be blended in the fuel. In a paper from Environment Australia discussing this issue (Environment Australia, 2002) it is pointed out that ethanol-gasoline blends with 10 % ethanol content are already available on the market, while the process to set environmental standard for gasoline should allow only 7.8 % ethanol in gasoline (i.e. 2.7 % oxygen by weight instead of 3.5). Furthermore, ethanol blends should have to meet the Reid Vapour Pressure requirements, which according to the standards should be <62 kPa in the area around Sydney, <67 kPa in Perth and <76 kPa in Queensland during the summer months according to Hellens (2002) of BP Australia.

#### 8.5. Theoretical Discussion on Vapour Pressure Using Raoult's Law

For liquid-liquid solutions where both components – in this case gasoline (gas) and ethanol (eth) – are volatile a modified Raoult's law applies.

$$P_{\text{total}} = P_{\text{gas}} + P_{\text{eth}} = \chi_{\text{gas}} P_{\text{gas}}^0 + \chi_{\text{eth}} P_{\text{eth}}^0 ; \chi_{\text{gas}} + \chi_{\text{eth}} = 1$$

Where  $P_{\text{total}}$  represents the total vapour pressure of a solution containing gasoline and ethanol,  $\chi_{\text{gas}}$  and  $\chi_{\text{eth}}$  are the mole fractions of gasoline and ethanol, respectively, and  $P_{\text{gas}}^0$  and  $P_{\text{eth}}^0$  are the pressures of the “pure” solutions. As gasoline is a mixture of chemical compounds and not a pure compound, only a theoretical discussion can be applied. However, in Figure 8.3 the vapour pressure of a gasoline-ethanol fuel blend is shown as a function of the ethanol mole fraction ( $\chi_{\text{eth}}$ ), based on the same primary data as used in Figure 8.1. The ethanol mole fraction was calculated using a “theoretical” calculated mean molecular weight of gasoline. The theoretical mole fraction of gasoline in the ethanol-gasoline blend was calculated using information on the percentage (by weight) of carbon and hydrogen in the gasoline. The estimated weight percentages used for carbon and hydrogen in gasoline are 87 and 13, respectively, accordingly to Hsieh et al. (2002). Using these values as input data a theoretical molecular formula of  $\text{C}_{15}\text{H}_{26}$  can be calculated for gasoline, consisting of  $\approx 87$  percent (w/w) carbon and  $\approx 13$  percent (w/w) hydrogen. In Figure 8.3 a positive deviation from Raoult's law can be seen, which can be attributed to the ethanol and gasoline interactions in the blend being weaker than the interactions among the molecules as neat liquids. Molecules in the blend have a higher tendency to reside in the gas phase, thus increasing the vapour pressure and leading to a positive deviation from Raoult's law, as shown in Figure 8.3.



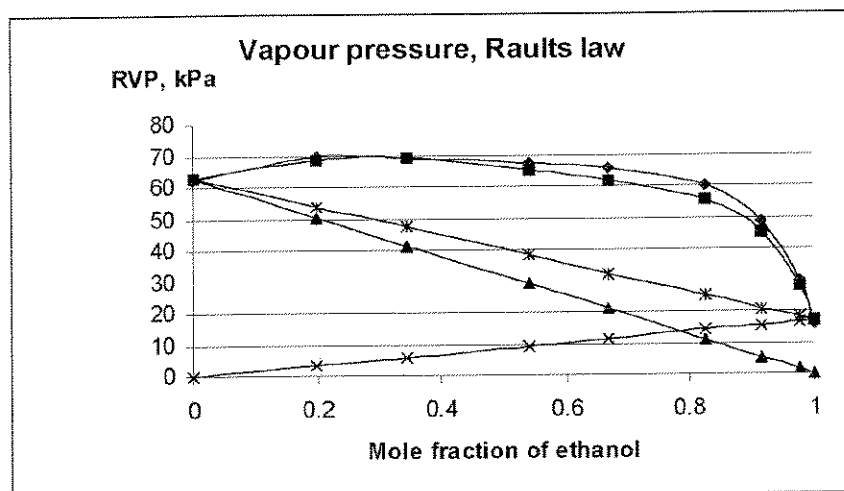


Figure 8.3. Reid Vapour Pressure (■Furey and Jackson, 1977; ◆DOE, 1991) as a function of the mole fraction of ethanol ( $\chi_{eth}$ ) blended in gasoline. X Ethanol RVP, Δ gasoline RVP, \* gasoline/ethanol blend of ideal solution.

## 8.6. Findings

- When ethanol is added to gasoline the vapour pressure of the resulting blend increases. The highest RVP is reached at a blending with approximately 10 % ethanol. Increasing the ethanol content above 10 % reduces the RVP, and at levels of 20 to 40 % ethanol (depending on the specification of the gasoline used) the RVP of the blend returns to the original level of the gasoline. Further increases in ethanol content will further decrease the RVP of the blend to levels below the original RVP of the gasoline used.
- Increased RVP may increase VOC emissions, depending on the type of evaporative emission control system used. However, no direct correlations between the gasoline vapour pressure and the exhaust VOC emissions from vehicles have been found.
- RVP-adjusted gasoline that is used for blending with ethanol, but still fulfils the RVP requirements set by EN 228 specifications, will have a lower energy content than gasoline that is not so adjusted
- Increased vapour pressure of a fuel may affect the drivability of the vehicle at high ambient temperatures, i.e. vapour lock may occur. It may also affect hot engine start ability.
- There is not much data from Swedish or European investigations on the effects of increased fuel vapour pressure on evaporative and tailpipe emissions. This issue is currently being investigated in an EU project, but no data or reports arising from it have been published to date.
- It is difficult to apply data from USA directly to Swedish or European conditions, since the gasoline used in the USA is quite different from Swedish/European gasoline standards. Gasoline standards applied in the USA are designed to solve problems such as poor air quality in city centres and the formation of tropospheric ozone, which are not always prioritised in Europe. Furthermore, the data from the USA can be mutually contradictory.
- There are very few data on emissions from Brazil regarding vehicles running on neat ethanol or ethanol gasoline blends. However, since the lowest ethanol content of the Brazilian fuel blends is 20%, the evaporative emissions from the vehicles are limited.

## 9. RISK FOR EXPLOSIONS AT LOW AMBIENT TEMPERATURES

McArragher (1996) discussed the minimum Reid Vapour Pressure required to ensure that the upper flammability limit of gasoline vapour is exceeded; a critically important safety issue (McArragher, 1996). This means that the head space in a tank should be saturated with gasoline vapour at a greater partial pressure than the upper flammability limit for a gasoline-air mixture, thus avoiding the risk for explosion. However, at low RVP and low ambient temperatures there is a risk that the headspace in a tank will be saturated with gasoline vapour which is under the upper flammability limit of the gasoline-air mixture, which is then an explosive chemical mixture. Blending up to approximately 10 % ethanol in the gasoline increases the initial RVP of the neat gasoline (Figure 8.1), suggesting that it should reduce the risk for a flammable mixture forming. If the ethanol content is increased above approximately 10 % the RVP of the gasoline/ethanol blend is lowered (Figure 8.1). At approximately 25 % ethanol, the gasoline-ethanol blend has approximately the same RVP as the neat gasoline. This means that use of ethanol contents higher than approximately 25 % will increase the risk that vapour will form with pressures under the upper flammability limit. According to the Swedish Rescue Services Agency (SRSA, 2004) there is no difference between gasoline and ethanol-blended gasoline from a legal perspective in terms of the risk for flammability or explosion. However, a concern raised by the SRSA is that ethanol can adversely affect the foam used by fire fighters, although ethanol-resistant foam is available. Thus, this potential problem can be overcome by informing local fire stations about the presence and locations of ethanol-blended gasoline filling stations.

## 10. LIFE CYCLE ANALYSIS (LCA) OF GASOLINE AND ETHANOL BLENDS

Life Cycle Analysis is a tool for analyzing and assessing environmental consequences of human actions, originally used to address product-related environmental issues. In LCA a product is followed from “cradle to grave” i.e. from raw material acquisition, through production, use and waste disposal. By assessing all of the industrial processes associated with manufacturing a given product, sub-optimization can be avoided, with respect to issues such as whether a raw material can be replaced with a less toxic one without increasing the total environmental impact due to changes in transportation distances or modes, and whether production of the new raw material (or substitution of a product with a similar one) will generate more or less toxic emissions

The ISO standard for LCA (ISO 14040, 1997) defines it as a “technique for assessing the environmental aspects and potential impacts associated with a product”, by:

- Compiling an inventory of relevant inputs and outputs of its production system.
- Evaluating the potential impacts associated with those inputs and outputs.
- Interpreting the results of the inventory and impact assessment phases in relation to the objective of the study.

LCA can be used to assess and compare, in a “cradle to grave perspective”, effects of using different vehicle fuels, such as gasoline, bio ethanol and bio ethanol-blended gasoline. The results may elucidate the “total” effects on the climate, environment and health of replacing gasoline to varying degrees by bio ethanol. However, when using LCA for assessment/comparison of different situations it is important to apply the same system boundary and framework conditions consistently. Otherwise, the LCA will not give reliable answers to the questions posed. For example, in response to a request by the Swedish Alternative Fuel Committee, Magnus Blinge of Chalmers University of Technology, Gothenburg (Blinge, 1996) compared about 20 different LCAs related to conventional and alternative vehicle fuels. One of Blinge’s main conclusions was that it was not possible to make a good comparison between these LCAs or to extract relevant average emission data concerning production, vehicle use etc. from them, largely because of small differences between them in terms of parameters such as the test vehicles (age and engine/vehicle configuration) and the test cycles used.

### *10.1. LCA in the Context of This Project*

The main purposes of the literature study related to LCAs within the BIFF-project were to search for, and examine, LCAs that included assessments of as many as possible of the following:

- The environmental and health effects of emissions from the use of neat gasoline and various ethanol-gasoline blends, ranging from 5 to approximately 20 % ethanol.
- Both vapour-pressure adjusted gasoline (i.e. gasoline fulfilling RVP requirements even after blending with ethanol) and unadjusted gasoline (with which blends would not meet such requirements).
- Emissions not only of carbon dioxide and/or other greenhouse gases, but also of regulated emissions and, as far as possible, other unregulated constituents.

- Potential differences in the emissions associated with various ethanol blending levels in different types of gasoline (RVP-adjusted and unadjusted).
- Changes in emissions from sensitive “emission points” from harbour/refinery to vehicle/tailpipe due to use of ethanol-gasoline blends with various ethanol contents and, if possible, identification of the best point in the chain for blending ethanol into gasoline, to minimise evaporative losses.
- If (and if so how) switching from the use of RVP-adjusted gasoline to unadjusted gasoline (allowing increases in vapour pressure) in gasoline-ethanol blends would affect the overall climatic, environmental and health impact.

A further objective of the work was to find out if LCAs, such as those mentioned above, carried out in the USA and other countries could provide a reasonable basis for predicting life-cycle changes in emissions that would follow the use of 5 to 20 % ethanol blends with gasoline, and fuels for use in Otto engines, and their impact (especially on the environment and health), under Swedish or European conditions. However, it was (and is) essential to remember that basing predictions on LCAs is likely to be difficult, or even impossible, unless the system boundary and framework conditions are very similar.

## ***10.2. LCA Studies for Ethanol in Neat Form or Blended with Gasoline***

### **USA**

The literature survey revealed that many LCAs have been carried out on the production and use of ethanol, mostly in the USA, under typical American conditions, e.g.:

- The raw materials for the production in the USA are often corn or corn residues.
- The vehicle parameters used in the LCA calculations are generally typical for engines/vehicles sold in the USA 5 to 10 years ago.
- The conventional fuel used in the comparisons is generally common US gasoline, which is not the same as European and less than that Swedish gasoline. In addition, the gasoline quality differs between regions/states in the USA and the US authorities have established special gasoline qualities for areas with special air quality problems, the so-called non-attainment areas (with respect to CO or tropospheric ozone). This means gasoline qualities with a minimum level of oxygen or a minimum level of added oxygenate (MTBE or ethanol), gasoline with a maximum level of vapour pressure (low vapour pressure gasoline, LWG) or gasoline with a maximum vapour pressure and low level of specific compounds, such as benzene and aromatics, reformulated gasoline (RFG).

### **Examples of such LCAs include:**

- Fuel-Cycle Fossil Energy Use and Greenhouse Gas Emissions of Fuel Ethanol Produced from U.S. Midwest Corn, Michel young, Christopher Saricks and May Wu, Argonne National Laboratory, US, 1997 (Young et al., 1997)
- Effects of Fuel Ethanol Use on Fuel-Cycle Energy and Greenhouse Gas Emissions, M Wang, C Saricks and D Santini, Argonne National Laboratory, USA (Wang et al., 1999).

However, since these LCAs were based on conditions specific for the USA there are various difficulties in using them as a basis for predictions related to Swedish and/or European conditions other than merely giving hints about likely results.

Furthermore, the LCAs that have been found mostly focused on emissions of carbon dioxide, and sometimes other greenhouse gases, but LCAs seldom consider emissions of regulated or other non-regulated constituents.

## Europe

For European conditions General Motors, together with Argonne National Laboratory, published a report entitled “Well-to-Wheel Energy use and Green House Gas Emissions of Advanced Fuel/Vehicle System – A European Study” The work was carried out with BP, ExxonMobil, Shell and TotalFinal Elf as active participants, and is a complement to a similar study for North American conditions published in 2001 (GM 2001). However, as can be seen from the title this LCA-study only covers greenhouse gases and energy use.

Another LCA related to European conditions was jointly undertaken by CONCAWE, EUCAR and the EU-Commissions/Joint Research Centre, as reported in “Well-to-Wheel Analysis of Future Automotive Fuels and Power Trains in the European Context” (Concawe 2004). This report also focuses on the emissions of greenhouse gases, as do two other European LCAs on bio fuels/ethanol. One carried out by Patyk and Reinhardt, of the Institut für Energie und Umweltforschung, Heidelberg, Germany, (Patyk and Reinhardt, 2002), entitled “Life Cycle Analysis of Bio Fuels for Transportation used in Fuel Cells and Conventional Technologies under European conditions”. The other, carried out by the French authority for environment and energy, ADEME, together with Ecobilan, PricewaterhouseCoopers and DIREM, was called “Energy and Greenhouse Gas Balances of Bio Fuels Production Chains in France, and was published in December 2002 (ADEME, 2002).

## Sweden

Several LCAs have been carried out on the production and use of alternative vehicle fuels under Swedish conditions, focusing on (or at least including) ethanol. In 1997, Magnus Blinge, of Chalmers University of Technology, Gothenburg, carried out an LCA on different alternative fuels following a request from the Swedish Transportation Research Board (Blinge et al., 1997). This LCA, despite being relatively old, and not based on the latest data, information and technology, still seems to be one of the best. It also covers non-regulated emissions. However, in addition to being old, the results are primarily valid for Swedish conditions and not applicable to the rest of Europe.

Another Swedish LCA that is specifically related to Swedish conditions is Agro Ethanol’s LCA on the annual production of 50 000 m<sup>3</sup> grain-based ethanol at the Agroetanol AB production plant outside Norrköping. However, this LCA is focused solely on emissions of greenhouse gases.

## Other countries

Two LCAs from countries outside Europe and the US are:

- Comparison of Transport fuels carried out by Beer and co-workers, the Australian Greenhouse Office, The University of Melbourne (Beer et al., 2002).
- Assessment of Greenhouse Gas Emissions in the Production and Use of Ethanol in Brazil, Government of the state of Sao Paulo, carried out by Isaias de Carvalho and co-workers. (I Carvalho et al., 2004).

Both of these LCAs are concerned with emissions of greenhouse gases and energy efficiency.

In addition, of course, LCAs have been carried out in other parts of the world, including China (see below), India and Canada, but these have also focused mainly on emissions of greenhouse gases with clear country-specific framework conditions, largely concerning the raw material.

### ***10.3. Discussion***

LCAs on the production, distribution and use of a vehicle fuel such as ethanol is often carried out with country-specific framework conditions such as the sources and nature of the raw material used to produce the fuel.

In most of the LCAs carried out to date on ethanol, “neat” ethanol for FFVs, 85 % ethanol and 15 % gasoline (E85), or ethanol-gasoline blends with low alcohol contents (5 % or occasionally 10 %; E5 or E10), are compared with neat gasoline. LCAs comparing blends with higher ethanol contents, up to 20 or 30 % for example, are scarce.

Concerning the parameters studied in LCAs on the production, distribution and use of alternative fuels/ethanol most have mainly focused on their climatic impact, especially emissions of carbon dioxide and, occasionally, emissions of other greenhouse gases.

LCAs that consider regulated emissions are not common. The investigation by Blinge and co-workers. (Blinge et al. 1997) is an exception, as is the “Economics, Environment and Energy Life Cycle Assessment of Automobiles Fueled by Bio-ethanol Blends in China”, study by Zhiyuan Hu and coworkers of Shanghai Jiao Tong University, China (Zhiyuan et al., 2004).

Furthermore, there have been few studies related to non-regulated emissions, and they are difficult to find.

To summarize:

- It is difficult to find LCAs that meet the criteria sought here.
- It is difficult to draw general conclusions concerning specific emissions due to the production, distribution and use of ethanol as vehicle fuels from a number of different LCAs because of differences in their system boundaries and framework conditions.
- It is difficult to use LCAs that have been published to date to predict general conditions for situations that were not foreseen, or considered, when they were carried out.

Although it is difficult to find the kind of LCA sought for and described in chapter 4.9.2, there is at least one example of an LCA in which different types of gasoline were examined that could be used as a procedural model for LCAs considering ethanol blends of RVP-adjusted and unadjusted gasoline. The study was performed by Teresa Mata and co-workers of the University of Porto, Portugal (Mata et al., 2003).

In the cited LCA, a life cycle analysis or assessment compared the potential environmental impact of various gasoline blends that all met the same octane and vapour pressure specifications. The system boundaries were set to include the refinery process, but exclude the fuels’ use in a vehicle. For the chain from refinery to refueling of the vehicle seven stages were defined and emission factors were calculated. Several types of gasoline that differed in their specifications, but fulfilled standard octane number and RVP requirements, were compared in terms of their potential environmental impact due to hydrocarbon emissions. The results of the

study showed that since the blending components such as alkylate, cracked gasoline and reformat have different octane numbers and vapour pressures, as well as differing in their potential environmental impact, some gasoline blends are less detrimental for the environment than others.

#### **10.4. Findings**

LCAs are difficult to find, worldwide or in Europe/Sweden that:

- Have relevant framework conditions (modern engine systems, relevant fuel specifications etc).
- Consider the emissions not only of greenhouse gases but also of regulated and other non-regulated constituents.
- Compare regulated and non-regulated emissions (tailpipe emissions and evaporative emissions) from a well-to-wheel perspective and their impact on the environment and health from the production, distribution and use of gasoline with blends of RVP-adjusted and unadjusted gasoline with 5 to 20 % ethanol.

A number of LCAs have been carried out (mainly but not solely in the USA), but they have applied more or less country-specific framework conditions with respect to the raw material used for the ethanol production and specific gasoline specifications. They have also often focused (as have most LCAs on the production, distribution and use of other alternative fuels) on the emissions of greenhouse gases. From a European or Swedish perspective, LCAs carried out in the USA or other parts of the world probably differ too much in their framework conditions to provide a relevant basis for predictions under European/Swedish conditions.

To obtain information concerning whether (and if so, how) evaporative emissions and tailpipe emissions might differ, from a well-to-wheel perspective, it seems necessary to carry out a new LCA. Such an LCA could be structured similarly to that of Mata and co-workers (Mata et al. 2003), but with specific Swedish framework conditions.

Such an LCA should focus on:

- Ethanol blended gasoline with ethanol contents in the 5 to 20 % range.
- Gasoline fulfilling RVP conditions in Europe/Sweden.
- Gasoline not fulfilling the RVP conditions. This implies accepting an increased RVP.
- Besides carbon dioxide, other greenhouse gases and both regulated and non-regulated emissions should be measured.

If possible the LCA should include some kind of evaluation concerning the extent to which different types of canisters could reduce the evaporative emissions from the vehicle and the extent to which they would reduce the total volume of emissions.

## 11. CONCLUSIONS AND RECOMMENDATIONS

Please note that conclusions from the literature study are written in regular font (Times New Roman) and recommendations by the authors of the present report are written in italic.

American car manufacturers have agreed to accept the use of blends with up to 10 % ethanol in gasoline in their vehicles, without changing the warranty conditions. Many car manufacturers in Europe and Japan sell vehicles in North America. *Therefore, the design of currently available on the European market, including Sweden, may allow the use of blends with at least 10 % ethanol in gasoline.*

A conclusion which can be drawn from the literature study is that newer models of vehicles are more tolerant to changes in the composition of fuels such as a blend of 10 % ethanol in gasoline. One problem that may apply to older vehicles is that alcohol tends to react with rubber. Owners of such cars should refrain from using alcohol blended gasoline. Many authors of papers dealing with alcohol fuels claim that the main cause of reported problems of using alcohols, especially methanol, as a fuel for vehicles is that they have often been used in older cars. *Further studies of the vehicle fleet in Sweden may be needed to generate information about the implications of using gasoline blends with up to 10 % ethanol for older cars which may be less tolerant to them than newer models.*

*It is difficult to apply data from investigations carried out in other countries directly to Swedish conditions since many variables differ from country to country, especially in terms of the fleet of vehicles, the fuels, emission regulations and certain other factors.* In addition, some investigations evaluated in the present report have given contradictory results. However, *updated exhaust emissions (of both regulated and unregulated compounds) from neat gasoline and ethanol gasoline blends should be characterized as described in the present report in tests at both ambient temperature of 20 °C (in accordance with current certification procedures) and lower temperatures, e.g. -20 °C.*

*Start ability and drivability at low ambient temperatures such as -20 °C are important variables to investigate due to the harshness of Swedish winters.*

Methods for sampling and analysing exhaust emissions have not been adequately developed for alternative fuels in general since traditional sampling and analysis methods were developed for characterizing emissions from traditional fuels such as gasoline and diesel oil. *There is a need to develop and update methods for sampling and analysing vehicle exhaust emissions generated from the combustion of alternative fuels.*

The percentage of ethanol in gasoline blends evaluated should primarily be in the range of 10 % as this could be the first upper target. *Higher than 10 % contents of ethanol in gasoline are expected to be of more importance after the year 2010.*

Investigations and evaluations conducted for the American Lung Association of Minnesota discussed in the present report have shown that the sulphur content of the fuel has a considerable impact on both regulated and unregulated emissions. *Therefore, data on emissions generated using fuels with relatively high sulphur contents cannot be directly applied to Swedish*



conditions, since Swedish gasoline standards have allowed only 10 ppm sulphur since January 2005.

*There is a need for updated emission factors for both regulated and unregulated exhaust emissions from "modern" vehicles running on neat gasoline and ethanol-blended gasoline. Besides measurements obtained following standard procedures, tests at low ambient temperatures (-20 °C) should also be included. Emission factors are needed for emission inventories, which provide a basis for evaluating health and environmental effects.*

*Local fire stations should be informed about the presence and location of ethanol blended gasoline filling stations to ensure the use of ethanol-resistant foam in the case of fire. This is also an important issue to consider if fires occur in vehicles running on these fuels, since their fuel tanks will contain ethanol/gasoline blends.*

### **11.1. Fuel Reid Vapour Pressure**

When an alcohol is blended with gasoline the vapour pressure of the blended fuel will increase (and considerably more for methanol than for ethanol). If ethanol is added, the RVP increases most rapidly with further additions in the ethanol content interval from 0 to 5 %, and it peaks at a blending level of approximately 10 % ethanol. The RVP then declines with further increases in the ethanol content, and at a level of 20 to 40 % ethanol (depending on the specification of the neat gasoline used) the RVP of the blend returns to the original level of the base gasoline. A further increase in ethanol content will then reduce the RVP of the blend to levels lower than that of the gasoline used.

Increasing RVP may increase the VOC emissions, depending on the type of evaporative emission control system used. *There is a need for updated emission factors for evaporative emissions from "modern" vehicles running on ethanol mixed with gasoline (5 - 10 %), comparing emissions from the use of both RVP-adjusted and non RVP-adjusted gasoline. In addition to measurements of evaporative emissions according to the standard method, emitted hydrocarbons should be analysed to generate data for use in further evaluations. With such data it will be possible to: (i) evaluate whether the evaporative emission standards are met and (ii) to evaluate whether the emitted hydrocarbons will have an impact on the environment and health in Sweden.*

Increasing the RVP of a fuel may affect the drivability of the vehicle at high ambient temperatures, since it may cause vapour lock and may also affect hot engine starts. If a gasoline with an RVP at or close to the upper limit is mixed (commingled) with a gasoline containing ethanol, the upper limit allowed for RVP could be exceeded.

The chemical compound in gasoline that contributes most to the RVP is butane. By decreasing or increasing the butane content in gasoline the RVP can be reduced or increased, respectively.

Very few data have been found on evaporative emissions from Brazil regarding vehicles running on neat ethanol or ethanol gasoline blends. However, since the lowest ethanol content of Brazilian fuel blends is 20%, the evaporative emissions from the vehicles are limited.

## 11.2. *Regulated Emissions*

As the energy content (MJ/l) of ethanol-gasoline blends is lower than that of neat gasoline their use will probably cause fuel consumption to increase for the average driver.

The search for literature on the effects of ethanol blends on regulated emissions showed that very few data are available on emissions measured when using a blend of 10 % ethanol in gasoline. Since nearly all vehicles in Sweden are equipped with a three-way catalyst exhaust gas after-treatment system, data obtained in tests with such vehicles were of particular interest. The emission data found and discussed in this report are from investigations in Australia, Canada, England (UK), Sweden and the USA. One main drawback when collecting and studying data from different investigations is that the number of vehicles tested is often limited.

The Orbital Engine Company has carried out a series of investigations on vehicles fuelled with ethanol blended gasoline initiated by Environment Australia. Most of these investigations have focused on a blend of 20 % ethanol in two or three grades of gasoline produced for the Australian market. However, the investigations carried out by Orbital have been of great value for this project since a broad spectrum of emission data are presented in the reports and they discuss many aspects such as fuels, vehicles, catalysts, vehicle performance and wear. Data on regulated, unregulated and evaporative emissions have been gathered and presented. There is only one main drawback with the data from the extensive tests involved; the fuel (gasoline) used for the tests with blended fuel and the neat gasoline had sulphur contents of up to 150 and 500 ppm, respectively, according to available information.

Investigations and evaluations conducted for the American Lung Association of Minnesota have shown that sulphur in the fuel has a considerable impact on both regulated and unregulated emissions.

A report from Environment Canada compares emission data from tests on ethanol blended gasoline and neat gasoline. The ethanol contents in the blended fuels were 10, 15 or 20 %. When comparing data from the different ethanol blends with data from tests on neat gasoline no dramatic differences were seen.

Beside the investigations carried out in Australia the emission tests carried out at Harwell, England, on five vehicles fuelled with a blend of 10 % ethanol in gasoline are of some interest, firstly because a 10 % ethanol in gasoline blend was used, and secondly because the vehicles used were models that are also used in Sweden. Generally the emission levels were low and no significant differences in NO<sub>x</sub> emissions were found. Emissions of CO and PM were significantly reduced when the use of blended was compared with neat gasoline.

Only limited data have been found concerning evaporative emissions. However, in some relevant investigations it has been noticed that emissions via permeation have increased when using ethanol blended gasoline. This has been especially significant in the USA after the strengthening of the evaporative emission regulations, since new measures had to be introduced to comply with the standards. One of these measures was to shift to the use of steel tanks for the fuel and another was to use new and more reliable tubes in the fuel lines.

In a paper from the Transportation Office of Energy Efficiency in Canada it is said that blending 10 % ethanol in gasoline (E10) will result in the energy content of the fuel being 3 % lower than the energy content of the base gasoline used for blending. Since this decrease in energy content will be partly compensated by "improved combustion efficiency" of the ethanol blended fuel the

overall increase in fuel consumption when using E10 will be only 2 %. In comparison, increasing the speed of the vehicle from 100 km/h to 120 km/h increases fuel consumption by 20 %.

*In the present report it has been emphasised that the method used for measuring hydrocarbons (HC) in the exhaust from motor vehicles using an alcohol blended fuel are not satisfactory from a legal perspective since the emissions of unburned alcohol are included in the readings of the instrument (FID). Therefore there is an urgent need to develop an analytical method that can determine HC emissions which are not affected by other "non HC" compounds present in the exhaust.*

*For regulated emissions the recommendation is that a broader more detailed study of the emissions, especially in low temperature conditions should be carried out, and tests including evaporative emissions at low temperatures. The resulting figures could probably be used to evaluate the environmental and health effects of using ethanol blends.*

### **11.3. Unregulated Emissions**

*There is a need for updated emission factors of unregulated exhaust emissions. The components examined should include the chemical compounds and compound classes listed in the present report.*

The emissions of aldehydes (especially acetaldehyde and, to a lesser degree, formaldehyde) and alcohols from vehicles running on alcohol/gasoline blends are expected to increase. *There is no standard validated method for determining aldehyde and alcohol emissions from motor vehicles, so (an) appropriate method(s) must be developed (see also the conclusion and recommendation about HC emissions discussed above).*

Due to the gasoline dilution effect of adding ethanol the emissions of benzene, toluene, ethyl benzene and xylene from blends are lower than those from neat gasoline, which is beneficial from environmental and health perspectives.

From the literature it is not clear whether there is risk that emissions of quinones from gasoline-fuelled vehicles will increase as the ethanol content increases in a gasoline/ethanol blend. *Thus, it is recommended that a pilot investigation should be initiated to investigate if quinone emissions are related to the ethanol content of ethanol-gasoline blends.*

There is clear, general interest from a health perspective in particle emissions from vehicles in the literature examined. *It is recommended that particles emitted from vehicles fuelled with ethanol/gasoline blends should be thoroughly characterised chemically, and this characterisation should include measurements of their sizes and numbers.*

### **11.4. Performance and Wear**

During the study of the literature no evidence of serious engine wear and/or other material problems were found when a blend of 10 % ethanol in gasoline had been used. It has also been noted that this level of ethanol in gasoline has been used in the USA since the end of the 1970s. A blend of 10 % ethanol in gasoline has long been allowed in the USA by the car manufacturers without any serious restrictions on the warranties of their vehicles. Therefore, substantial experience of the use of ethanol blended gasoline has been collected over a long time. However, the limit for the ethanol content in gasoline has been set to 10 % under the warranty conditions.

Extensive tests and studies carried out in Australia have found that using an ethanol-gasoline blend with 20 % ethanol increased the wear and other damage to the fuel system of the vehicles, especially at high accumulated mileages. It has not been possible to verify whether this is linked to the fact that the sulphur content of gasoline in Australia is relatively high, since this possibility was not considered in the reports from Australia. In Sweden the sulphur content in gasoline has been reduced to a maximum of 10 ppm. A high level of sulphur in the ethanol blended fuel may affect the engine fuel system since there is a small amount of acetic acid in neat ethanol (a maximum of 0.0025 % by weight, according to AMSE 1114).

In the light of the findings concerning the engine wear and other observed problems associated with the use of 20 % ethanol in gasoline the Australian government has decided to limit the amount of ethanol in gasoline to 10 %. Representatives of the oil industry and car owners also favoured the 10 % limit.

In contrast to the experiences in Australia, a study conducted in Minnesota (USA), in which two blends of ethanol in gasoline (one with 10 % and the other with 30 % ethanol) were examined, found that the ethanol caused no serious wear problems. The project included both laboratory tests and field trials. Unfortunately, however, no emission data are available from these tests.

*In the 1970s and 1980s a quite extensive program was carried out in Sweden to study the effects of using alcohol blends in gasoline in motor vehicles. No such program has been established to collect experience and data regarding the use of ethanol blended gasoline since then. Therefore very few Swedish data are available.*

### **11.5. Life Cycle Analysis**

A number of LCAs have been carried out worldwide on the use of bio ethanol, but they are more or less based on country-specific framework conditions with respect to the production, distribution and use of alternative fuels. Furthermore, most of them focus solely on the emissions of greenhouse gases.

It can be concluded from the literature survey that LCA data with relevant framework conditions for the use of bio ethanol and bio ethanol mixed gasoline in a Swedish/European perspective are limited or lacking.

*A new LCA based on Swedish framework conditions should focus on ethanol-gasoline blends with alcohol contents ranging from 5 to 20 %. Furthermore, as well as greenhouse gases (carbon dioxide, methane and nitrous oxide), regulated and other unregulated emissions should be included in it. The impact on the environment and health, of the production, distribution and use of the blends should be considered. Such an LCA could be structured in a similar way to the LCA published by Mata et al. (2003), but using specific Swedish framework conditions. Furthermore, both RVP-adjusted and non RVP-adjusted gasoline should be included.*

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### 13. ABBREVIATIONS

API	American Petroleum Institute
B(a)P	benzo(a)pyrene
BRON	Blending Research Octane Number
BTEX	benzene toluene, ethyl benzene, xylene
CARB	California Air Resource Board
CH <sub>3</sub> CH <sub>2</sub> -OH	Ethanol
CO	Carbon monoxide
CONCAWE	The Oil Companies' European Association for Environment, Health and Safety in Refining and Distribution
DME	Dimethyl ether
DOE	Department of Energy
EIA	US Energy Information Administration
EFI	Electronic Fuel Injection
Eth	Ethanol
EU	European Union
EUCAR	European Council for Automotive Research and Development
Evap	Evaporative
E85	15% conventional gasoline and 85% ethanol
FBP	Final Boiling Point
FFVs	Flexible Fuelled Vehicle
FID	Flame Ionization Detector
Gas	Gasoline
Gasohol	A gasoline extender made from a mixture of gasoline (90%) and ethanol (10%; often obtained by fermenting agricultural crops or crop wastes) or gasoline (97%) and methanol, (3%)
GM	General Motors
GWP	Global Warming Potential
HC	Hydrocarbons
IBP	Initial Boiling Point
IEA	The International Energy Agency

IEA	International Symposium on Alcohol Fuels
JRC	EU Joint Research Centre
KPa	Kilo Pascal
LPG	Natural gas and Motorgas/Petroleum gas
MTBE	Methyl Teriary Buthyl Ether
MON	Motor Octane Number
NDIR	Nondispersive Infrared
NMOG	Non Methane Organic Gases
NO <sub>x</sub>	Nitrogen oxides
PAC	Polycyclic Aromatic Compounds
PAH	Polycyclic Aromatic Hydrocarbons
PAN	Peroxy acetyl nitrate
PULP	Perth unleaded petrol
Psi	Pounds per square inch
RFA	Renewable Fuels Association
RFG	Reformulated Gasoline
RON	Research Octane Number
RVP	Reid Vapour Pressure
RCGWE	Relative Contribution to the Global Warming Effect.
SEKAB	Svensk Etanolkemi AB
SPI	Swedish Petroleum Institute
STAB	Swedish Motor Fuel Technology Co.
STU	Swedish National Board for Technical Development
SHED	Evaporative Test Chamber (Sealed Housing for Evaporative Determination)
THC	Total Hydrocarbons
TWC	Three Way Catalyst
ULP	Unleaded petrol
US EPA	US Environmental Protection Agency
VOC	Volatile organic compounds
Vol %	Volume percent
VTT	Technical Research Centre of Finland

## 14. APPENDIX 1

### 14.1. Emission tests in Canada

The following five tables, A1 to A5, list emission data generated during the tests carried out in Canada and presented in section 7.2 of the main part of the report. As can be seen there is a considerable variation in emission levels from vehicle to vehicle. It is particularly noteworthy that the Grand Am and Silverado show higher levels of emissions than the other vehicles

Table A1. Emissions of CO when using neat gasoline and three different blends of ethanol.

Vehicle ⇒	Grand Am	Honda Insight	Silverado	Echo	Civic
US FTP cycle	CO g/km	CO g/km	CO g/km	CO g/km	CO g/km
0 % Ethanol	0.920	0.205	0.963	0.280	0.305
10 % Ethanol	0.808	0.218	0.740	0.261	0.273
15 % Ethanol	0.709	0.186	0.938	0.224	0.205
20 % Ethanol	0.777	0.143	0.740	0.242	0.155

Table A2. Emissions of HC when using neat gasoline and three different blends of ethanol.

Vehicle ⇒	Grand Am	Honda Insight	Silverado	Echo	Civic
US FTP cycle	HC g/km	HC g/km	HC g/km	HC g/km	HC g/km
0 % Ethanol	0.056	0.027	0.075	0.050	0.025
10 % Ethanol	0.068	0.027	0.068	0.050	0.021
15 % Ethanol	0.056	0.024	0.087	0.049	0.017
20 % Ethanol	0.060	0.024	0.068	0.051	0.021

Table A3. Emissions of NO<sub>x</sub> when using neat gasoline and three different blends of ethanol.

Vehicle ⇒	Grand Am	Honda Insight	Silverado	Echo	Civic
US FTP cycle	NO <sub>x</sub> g/km	NO <sub>x</sub> g/km	NO <sub>x</sub> g/km	NO <sub>x</sub> g/km	NO <sub>x</sub> g/km
0 % Ethanol	0.118	0.026	0.068	0.087	0.030
10 % Ethanol	0.131	0.033	0.081	0.087	0.032
15 % Ethanol	0.124	0.049	0.068	0.068	0.039
20 % Ethanol	0.124	0.068	0.081	0.068	0.033

Table A4. Emissions of CO<sub>2</sub> when using neat gasoline and three different blends of ethanol.

Vehicle ⇒	Grand Am	Honda Insight	Silverado	Echo	Civic
US FTP cycle	CO <sub>2</sub> g/km	CO <sub>2</sub> g/km	CO <sub>2</sub> g/km	CO <sub>2</sub> g/km	CO <sub>2</sub> g/km
0 % Ethanol	249.2	101.9	303.9	161.6	179.6
10 % Ethanol	244.3	105.0	305.8	162.8	176.5
15 % Ethanol	247.4	103.2	307.0	162.8	176.5
20 % Ethanol	248.6	100.1	307.0	161.0	175.3

Table A5. Fuel consumption when using neat gasoline and three different blends of ethanol.

Vehicle ⇒	Grand Am	Honda Insight	Silverado	Echo	Civic
US FTP cycle	FC l/10 km	FC l/10 km	FC l/10 km	FC l/10 km	FC l/10 km
0 % Ethanol	1.063	0.435	1.293	0.701	0.764
10 % Ethanol	1.077	0.463	1.346	0.720	0.783
15 % Ethanol	1.102	0.464	1.352	0.731	0.790
20 % Ethanol	1.144	0.460	1.410	0.739	0.803

## 14.2. Emission tests in UK

The following four tables, A6 to A9, list emission data generated during the tests carried out in England and presented in section 7.3 of the main part of the report.

In Tables A6, A7 and A8 the emission data and fuel consumption of interest are presented; the measurements of regulated emissions and fuel consumption in Table A6, and those of unregulated emissions in Tables A7 and A8. As can be seen there is considerable variation in emission levels from vehicle to vehicle. It can also be seen that some vehicles show an increase in emissions when ethanol blended fuel is used, while others show a decrease.

Table A6. Summary of regulated emissions for all tested vehicles

Vehicle 1 Toyota (Yaris) running on base gasoline fuel.

Drive cycle	CO <sub>2</sub>	CO	THC	NO <sub>x</sub>	PM	Fuel cons.
	g/km	g/km	g/km	g/km	g/km	g/km
Cold ECE	165.9	1.904	0.307	0.150	0.0059	53.55
Cold EUDC	110.7	0.512	0.018	0.027	0.0058	35.16

Vehicle 1 Toyota (Yaris) running on E10 fuel

Drive cycle	CO <sub>2</sub>	CO	THC	NO <sub>x</sub>	PM	Fuel cons.
	g/km	g/km	g/km	g/km	g/km	g/km
Cold ECE	162.6	2.787	0.323	0.108	0.0018	55.04
Cold EUDC	109.5	0.047	0.016	0.035	0.0011	36.04

Vehicle 6 Toyota (Yaris) (repeated) running on base gasoline fuel.

Drive cycle	CO <sub>2</sub>	CO	THC	NO <sub>x</sub>	PM	Fuel cons.
	g/km	g/km	g/km	g/km	g/km	g/km
Cold ECE	161.5	1.328	0.402	0.207	0.0083	51.99
Cold EUDC	107.1	0.465	0.038	0.024	0.0049	34.03

Vehicle 1 Toyota (Yaris) (repeated) running on E10 fuel.

Drive cycle	CO <sub>2</sub>	CO	THC	NO <sub>x</sub>	PM	Fuel cons.
	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>
Cold ECE	156.1	1.577	0.296	0.132	0.0084	52.26
Cold EUDC	106.1	0.425	0.019	0.029	0.0034	35.00

Vehicle 2 Vauxhall (Omega) running on base gasoline fuel.

Drive cycle	CO <sub>2</sub>	CO	THC	NO <sub>x</sub>	PM	Fuel cons.
	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>
Cold ECE	386.7	1.159	0.551	0.243	0.0058	123.04
Cold EUDC	211.7	0.225	0.005	0	0.0027	66.85

Drive cycle	CO <sub>2</sub>	CO	THC	NO <sub>x</sub>	PM	Fuel cons.
	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>
Cold ECE	323.3	0.422	0.011	0.006	0.0071	106.16
Cold EUDC	181.9	0.187	0.005	0.004	0.0042	59.70

Vehicle 3 Fiat (Punto) running on base gasoline fuel.

Drive cycle	CO <sub>2</sub>	CO	THC	NO <sub>x</sub>	PM	Fuel cons.
	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>
Cold ECE	200.6	4.891	0.447	0.211	0.0056	66.12
Cold EUDC	125.2	0.262	0.016	0.011	0.0005	39.63

Vehicle 3 Fiat (Punto) running on E10 fuel.

Drive cycle	CO <sub>2</sub>	CO	THC	NO <sub>x</sub>	PM	Fuel cons.
	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>
Cold ECE	191.0	4.157	0.402	0.217	0.0029	65.14
Cold EUDC	110.1	0.190	0.011	0.010	0	36.18

Vehicle 4 Volkswagen (Golf) running on base gasoline fuel.

Drive cycle	CO <sub>2</sub>	CO	THC	NO <sub>x</sub>	PM	Fuel cons.
	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>	<b>g/km</b>
Cold ECE	246.0	0.983	0.183	0.087	0.0202	78.24
Cold EUDC	132.2	0.059	0.004	0.006	0.0046	41.73

Vehicle 4 Volkswagen (Golf) running on E10 fuel.

Drive cycle	CO <sub>2</sub>	CO	THC	NO <sub>x</sub>	PM	Fuel cons.
	g/km	g/km	g/km	g/km	g/km	g/km
Cold ECE	226.5	0.773	0.135	0.095	0.0008	74.75
Cold EUDC	127.8	0.039	0.004	0.010	0.0011	41.89

Vehicle 5 Rover (416) running on base gasoline fuel.

Drive cycle	CO <sub>2</sub>	CO	THC	NO <sub>x</sub>	PM	Fuel cons.
	g/km	g/km	g/km	g/km	g/km	g/km
Cold ECE	250.6	8.246	0.604	0.422	0.0056	83.68
Cold EUDC	147.5	0.373	0.020	0.255	0.0036	46.70

Vehicle 5 Rover (416) running on E10 fuel

Drive cycle	CO <sub>2</sub>	CO	THC	NO <sub>x</sub>	PM	Fuel cons.
	g/km	g/km	g/km	g/km	g/km	g/km
Cold ECE	256.2	7.509	0.525	0.450	0.0074	88.35
Cold EUDC	146.2	0.841	0.026	0.302	0.0009	48.38

Table A7. Summary of FTIR emissions measurements for vehicles 4, 5 and 6

Vehicle 6 Toyota (Yaris) (repeat) running on base gasoline fuel.

Drive cycle	Methane	1,3-butadiene	Formaldehyde	Acetaldehyde	Nitrous oxide	Benzene
	mg/km	mg/km	mg/km	mg/km	mg/km	mg/km
Cold ECE	79.593	3.007	0.974	9.042	0.660	N/D*
Cold EUDC	13.173	0.326	0.288	1.003	0.095	3.124

Vehicle 6 Toyota Yaris (repeat), running on E10 fuel

Drive cycle	Methane	1,3-butadiene	Formaldehyde	Acetaldehyde	Nitrous oxide	Benzene
	mg/km	mg/km	mg/km	mg/km	mg/km	mg/km
Cold ECE	92.031	1.307	0.509	18.183	0.198	10.092
Cold EUDC	11.640	0.231	0.197	0.896	0.014	1.347

Vehicle 4 Volkswagen (Golf) running on base gasoline fuel.

Drive cycle	Methane	1,3-butadiene	Formaldehyde	Acetaldehyde	Nitrous oxide	Benzene
	mg/km	mg/km	mg/km	mg/km	mg/km	mg/km
Cold ECE	13.009	1.739	0.079	1.619	0.012	N/D*
Cold EUDC	0.602	0.104	0.009	0.078	0.004	0.003

Vehicle 4 Volkswagen (Golf) running on E10 fuel.

Drive cycle	Methane	1,3-butadiene	Formaldehyde	Acetaldehyde	Nitrous oxide	Benzene
	mg/km	mg/km	mg/km	mg/km	mg/km	mg/km
Cold ECE	11.977	1.120	0.074	4.365	0.388	N/D*
Cold EUDC	0.655	0.076	0.031	0.163	0.001	N/D*

Vehicle 5 Rover (416) running on base gasoline fuel.

Drive cycle	Methane	1,3-butadiene	Formaldehyde	Acetaldehyde	Nitrous oxide	Benzene
	mg/km	mg/km	mg/km	mg/km	mg/km	mg/km
Cold ECE	69.302	4.011	0.220	13.846	N/D*	N/D*
Cold EUDC	11.260	0.183	0.124	1.225	N/D*	N/D*

Vehicle 5 Rover (416) running on E10 fuel

Drive cycle	Methane	1,3-butadiene	Formaldehyde	Acetaldehyde	Nitrous oxide	Benzene
	mg/km	mg/km	mg/km	mg/km	mg/km	mg/km
Cold ECE	50.244	2.334	0.107	12.660	N/D*	N/D*
Cold EUDC	7.247	0.107	0.039	1.408	0.007	N/D*

\* No data presented.

Table A8. Summary 2 of FTIR emissions measurements for vehicles 4, 5 and 6

Vehicle 6 Toyota (Yaris, repeat) running on base gasoline fuel.

Drive cycle	Benzene	Ammonia	Formaldehyde	Acetaldehyde	Total PAHs
	mg/km	mg/km	mg/km	mg/km	µg/km
Cold ECE+EUDC	0.124	4.001	0.667	0.200	43.62*

Vehicle 6 Toyota (Yaris, repeat) running on E10 fuel

Drive cycle	Benzene	Ammonia	Formaldehyde	Acetaldehyde	Total PAHs
	mg/km	mg/km	mg/km	mg/km	µg/km
Cold ECE+EUDC	0.057	5.232	0.401	0.654	44.86*

Vehicle 4 Volkswagen (Golf) running on base gasoline fuel.

Drive cycle	Benzene	Ammonia	Formaldehyde	Acetaldehyde	Total PAHs
	mg/km	mg/km	mg/km	mg/km	µg/km
Cold ECE+EUDC	0.347	4.567	0.114	0.049	113.71*



Vehicle 4 Volkswagen (Golf) running on E10 fuel

Drive cycle	Benzene	Ammonia	Formaldehyde	Acetaldehyde	Total PAHs
	mg/km	mg/km	mg/km	mg/km	µg/km
Cold ECE+EUDC	0.056	2.755	0.072	0.178	30.22 *

Vehicle 5 Rover (416) running on base gasoline fuel.

Drive cycle	Benzene	Ammonia	Formaldehyde	Acetaldehyde	Total PAHs
	mg/km	mg/km	mg/km	mg/km	µg/km
Cold ECE+EUDC	0.357	7.788	0.214	0.532	42.57*

Vehicle 5 Rover (416) running on E10 fuel

Drive cycle	Benzene	Ammonia	Formaldehyde	Acetaldehyde	Total PAHs
	mg/km	mg/km	mg/km	mg/km	µg/km
Cold ECE+EUDC	1.818	18.826	1.298	1.493	66.17*

\* Average value for Cold ECE+EUDC and the following driving cycles: WSL Congested, WSL Urban,

## **15. APPENDIX 2**

### ***15.1. Evaporation Test of Two Ethanol Blended RON 95 Summer Gasolines***

Separate report from AVL MTC AB.

# **Evaporation Test of Two Ethanol Blended RON 95 Summer Gasolines**



Magnus Henke

**2005-04-29**

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## 1 SUMMARY

The evaporative emissions from two summer gasoline fuels (with Reid Vapour Pressures, RVPs, of 63 kPa and 70 kPa, respectively) blended with low percentages of ethanol (0%, 5%, 10% and 15%) have been measured in a VT Shed. For reference purposes E85 (85% ethanol) was also measured in the same manner.

In the tests, a half-filled container prepared with an opening for the gaseous compounds to pass through was placed on its side in the shed at an ambient temperature of 45 °C. Each fuel was stabilized at 0°C at the beginning of the test and had a final temperature of about 40°C. Total hydrocarbon (THC) emissions were monitored at appropriate intervals through the use of a Flame Ionization Detector (FID) installed in the VT Shed and a number of components of interest of the same test fuel were sampled throughout the tests with a mass spectrometer (MS).

The FID data showed that evaporated THC levels ranged from 200 ppm for the unblended gasoline with the low (63 kPa) RVP, to 340 ppm for a 10% mix of ethanol in the high RVP (70 kPa) gasoline.

Test results showed that the RVP rises sharply when ethanol is first added to the fuels and peaks at ethanol contents between 5 and 10%.

Butane was the main component that vaporized during the tests, as expected since the vapour pressure of commercially supplied gasoline is primarily adjusted to meet regulated standards by adjusting butane levels.

The evaporation of ethanol was influenced both by its content in the tested blends and by the consequent changes in vapour pressure (RVP), and thus showed slightly different evaporation patterns from the other components.

The addition of ethanol also caused the evaporation of all the remaining components to increase by approximately the same factors as the butane.

Evaporation from the blends with the high RVP (70 kPa) base gasoline was stronger than the evaporation from the gasoline with the lower RVP (63 kPa), although there was some overlap.

## 2 INTRODUCTION

To meet the requirements of the European Directive designed to promote the use of biofuels (2003/30/EC) Sweden has to substantially increase the production or imports of renewable fuels. Legislation has to make it easier, and in some cases possible, to market and use these hybrid fuels.

To meet these goals in a short time steps have to be taken to ensure that the introduced fuels are usable by the current vehicle fleet. The only plausible way to reach this goal is to increase the amount of these fuels blended in today's conventional fuels. Previous experience suggests that alcohols should be added to gasoline for this purpose.

Methanol and ethanol are the main alternative fuels that have been tested on a relatively large scale, both as blended and pure fuels. This report focuses on the use of ethanol.

One problem related to the use of ethanol in gasoline is the increased vapour pressure caused by the alcohol when mixed in relatively low proportions with gasoline. Blends of around 10% are of particular concern today.

In the study reported here, the partial vapour pressures of ethanol and selected components of gasoline were measured in tests with blends of two base gasolines (with Reid Vapour Pressures, RVP, of 63 kPa and 70 kPa, respectively) and ethanol contents of 0%, 5%, 10% and 15%.

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### 3 EXPERIMENTAL

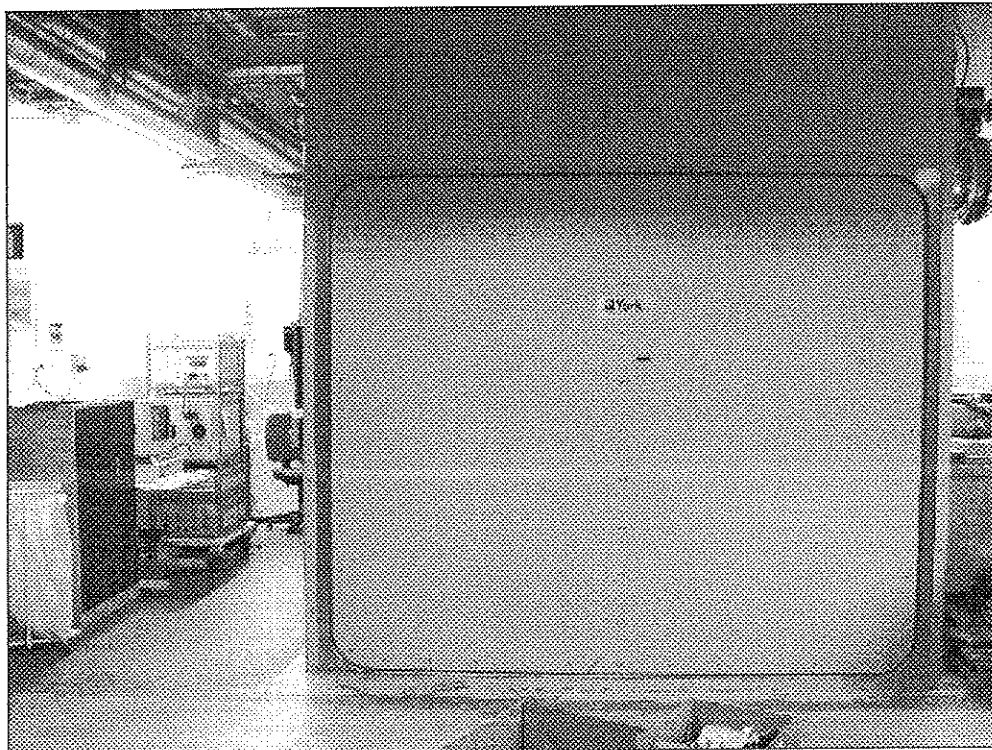
#### 3.1 Test Facilities

All tests were performed at AVL MTC in Haninge, Sweden, in February 2005.

The AVL MTC Motor test centre is an accredited laboratory for automotive testing and has been in operation for approximately 15 years. AVL MTC has experience of more than 10 years of testing for the Swedish Environmental Protection Agency and the Swedish National Road Administration.

#### 3.2 Testing equipment

All tests were performed using a gas-proof test container (not the fuel container mentioned below) in which the evaporative behaviour of whole cars is normally tested. It is called a VT shed as both its volume and temperature are controlled. A standard component of this kind of equipment is a Flame Ionization Detector (FID) for measuring the total emitted hydrocarbons. This instrument, along with an Air Sense Mass Spectrometer, was used for the tests.



Picture 1 – VT Shed Container with Mass Spectrometer to the left

### 3.3 Fuels

The base fuels used were identical mixtures, except for their contents of the Reid Vapour Pressure (RVP)-regulating compound butane, a larger quantity of which had been removed from the 63 kPa RVP fuel. Adjusting the RVP in this way is a standard procedure when commercially preparing gasoline that is to be blended with ethanol, to ensure that the vapour pressure of the final blend does not exceed specified limits.

#### 3.3.1 Specifications

PREEM RAFFINADERI AB Certificate of Quality			
Product Code:	SM9570	Vessel / Batch:	Blend95.041222.S165
Nomination number:	Blend95.041222.S165	Destination:	
Testdate:	2004 Dec 22	Account:	
Tank:	S165	Delivery Date:	
Revised Issue:		Sample Number:	2004040229
<b>Blend 95 RVP 63</b>			
Properties	Results	Units	Ref. Test Methods
Appearance at 20°C	BRIGHT AND CLEAR		Visual inspection
Aromatic content	38,5	% V/V	ASTM D 1319-95
Benzene content	0,8	% V/V	EN 238:1996
Colour	Undyed		Visual inspection
Cu strip corrosion(3h at 50°C)	1A		EN ISO 2160:1998
Density at 15°C	754,7	kg/m <sup>3</sup>	EN ISO 12185:1996
Dist. IBP	32,0	°C	prEN ISO 3405:1998
Dist. 10% Evap.	55,0	°C	PREN ISO 3405:1998
Dist. 50% Evap.	103,5	°C	PREN ISO 3405:1998
Dist. 90% Evap.	151,5	°C	PREN ISO 3405:1998
Dist. FBP	198,0	°C	prEN ISO 3405:1998
Dist. Residue	1,0	% V/V	PREN ISO 3405:1998
Gum content (solvent washed)	< 4	mg/100ml	EN ISO 6246:1997
Lead content	< 1,00	mg/l	EN 237:1996
Octane Nr. MON	84,8	-	EN 25163:1993
Octane Number RON	95,2	-	EN 25164:1993
Olefine content	8,0	% V/V	ASTM D 1319-95
Oxyg. MTBE content	< 0,5	% V/V	EN 1601:1997
Phosphorous content	< 1,00	mg/t	SS 15 51 80 1989
Sulphur content	30	mg/kg	EN ISO 8764:1996
Vapour pressure (DVPE)	63,7	kPa	prEN 13016-1:1997
Water content	45	mg/kg	ASTM D 1744-92
Results according to ISO 4259			
This product meets the quality requirements according to customer's nomination.		Work by: Ingvar Nilsson Chemist in Charge: Ingvar Nilsson	
Telephone: +46 31 64 61 85			
Fax: +46 31 64 61 86		For Preem Raffinaderi AB, Gothenburg: <i>Ingvar Nilsson</i>	

Table 1. Gasoline Certificate of Quality (RVP 63 kPa)





M T C

Prepared  
Magnus HenkeDate - Rev  
2004-07-13Document - Ref  
Report <2005-05-30> <1>Page  
7 (20)PREEM RAFFINADERI AB  
Certificate of Quality

Product Code: SM9570  
Nomination number: BL9570.041230.FAT  
Testdate: 2004 Dec 30  
Tank: FAT  
Revised Issue:

Batch: BL9570.041230.FAT  
Destination:  
Account:  
Delivery Date:  
Sample Number: 2004041240

## Blend 95 RVP=70

Properties	Results	Units	Ref. Test Methods
Appearance at 20°C	BRIGHT AND CLEAR		Visual inspection
Aromatic content	37,7	% V/V	ASTM D 1319-95
Benzene content	0,8	% V/V	EN 238:1998
Colour	Undyed		Visual inspection
Cu strip corrosion(3h at 50°C)	1A		EN ISO 2160:1998
Density at 15°C	751,6	kg/m3	EN ISO 12185:1996
Dist. IBP	30,0	°C	prEN ISO 3405:1998
Dist. 10% Evap.	51,5	°C	PREN ISO 3405:1998
Dist. 50% Evap.	102,0	°C	PREN ISO 3405:1998
Dist. 90% Evap.	151,5	°C	PREN ISO 3405:1998
Dist. FBP	196,0	°C	prEN ISO 3405:1998
Dist. Residue	1,0	% V/V	PREN ISO 3405:1998
Gum content (solvent washed)	< 4	mg/100ml	EN ISO 6246:1997
Lead content	< 1,00	mg/l	EN 237:1996
Octane Nr. MON	84,8	-	EN 25163:1993
Octane Number RON	85,2	-	EN 25164:1993
Olefine content	8,0	% V/V	ASTM D 1319-95
Oxyg. MTBE content	< 0,5	% V/V	EN 1601:1997
Phosphorous content	< 1,00	mg/l	SS 15 51 80:1989
Sulphur content	28	mg/kg	EN ISO 8754:1995
Vapour pressure (DVPE)	70,0	kPa	prEN 13016-1:1997
Water content	45	mg/kg	ASTM D 1744-92

Results according to ISO 4259

This product meets the quality requirements  
according to customer's nomination

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Work by: Ingvar Nilsson

Chemist in Charge: Ingvar Nilsson

For Preem Raffinaderi AB, Gothenburg. *Ingvar Nilsson*

Table 2. Gasoline Certificate of Quality (RVP 70 kPa)

### 3.4 Blending & Storage

The test fuels were blended by personnel with a very good understanding of the test and the difficulties associated with it. Particularly close attention was paid to obtaining a uniform start temperature and making sure that no fuel was exposed to temperatures that might cause early vaporization. Therefore blending was performed in an area conditioned to a maximum of 0°C.

For the same reason, the fuel was stored in the conditioned area until just before the test. On average the transportation and preparation of the previously blended fuel before the tests took only 3 min. By the time the test was started the temperature of the gasoline had risen on average by 1.5°C.

### 3.5 Test procedure

Each test consisted of three major parts:

- Conditioning the fuel and filling the test container.
- The test procedure in the VT shed.
- Purging the VT shed.

#### 3.5.1 Conditioning:

The fuel was brought down to sub-zero temperatures before being poured into the special test container and taken into the test facility. In the test container the temperature of the fuel was monitored continuously. When the desired temperature was reached the container was taken into the VT shed and the test was started. -

#### 3.5.2 Test procedure in the VT shed

A specially prepared fuel container conditioned at 0°C was placed in the container whilst the VT shed itself was set to maintain a steady 40°C throughout the test. To make sure a uniform concentration was present throughout the entire volume of the VT shed, a small floor-mounted fan directed away from the fuel container acted as an "air mixer".

In the fuel container a small hole was drilled, which was plugged until the start of the test, when the container was set on its side, the hole was opened and a thermocouple was plugged in to monitor the fuel temperature during the test.

### 3.5.3 Purging of the VT shed

To ensure that the VT shed was rid of all residual vapour before a new test was started it had to be purged. This is a lengthy procedure which involves taking the shed to its maximum temperature for approximately an hour.

A graph displaying changes in temperature over time of all the tested blends is presented below (Figure 1). The rising traces represent the fuel container temperature and the steady traces the VT shed air temperature.

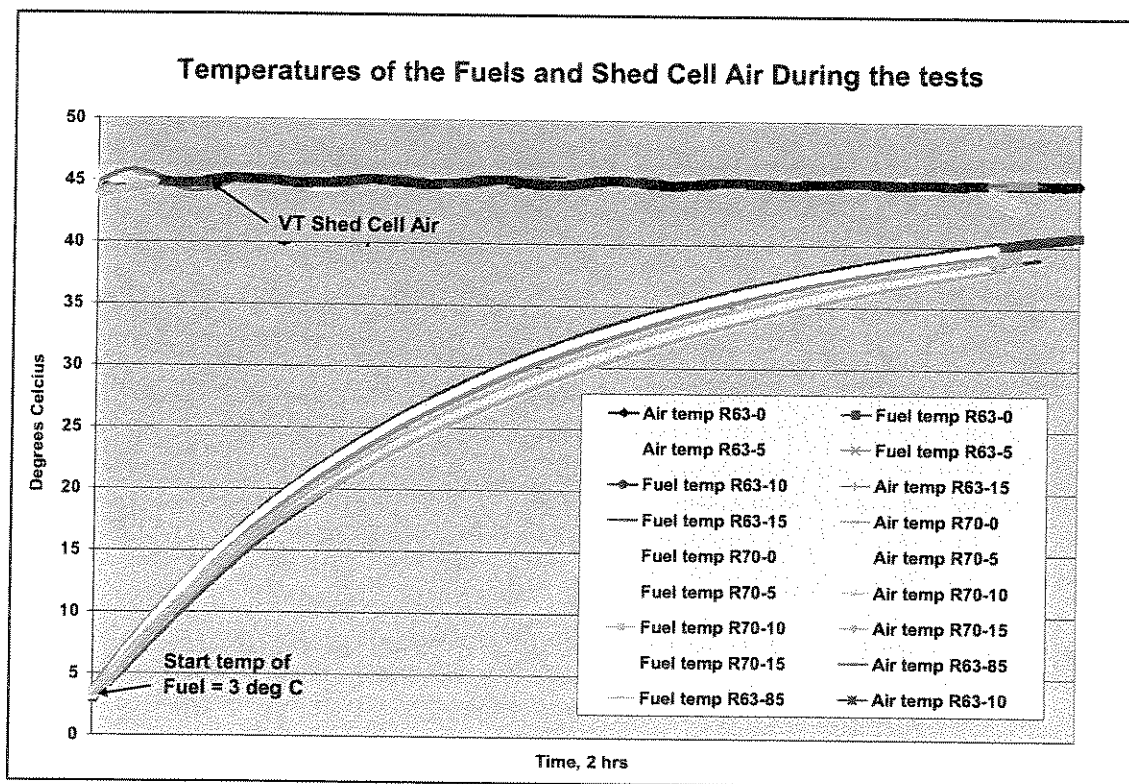


Figure 1 Temperature of the Fuels and VT Shed cell Air during the tests

### 3.6 Calibration

Both of the instruments used for measuring (the FID and MS) during this project were calibrated using certified pre-mixed gases to ensure quality. All calibration gases were delivered by Air Liquide and traceable in accordance to the standard of NIST.

## 4 RESULTS

Changes over time in the air levels of the measured constituents as the tests progressed are here presented in chart form to facilitate interpretation of the measurements. The final concentrations at the end of the tests are also presented in bar graph format at the end of this report to facilitate comparisons.

### 4.1 Changes over time in Hydrocarbon levels (FID).'

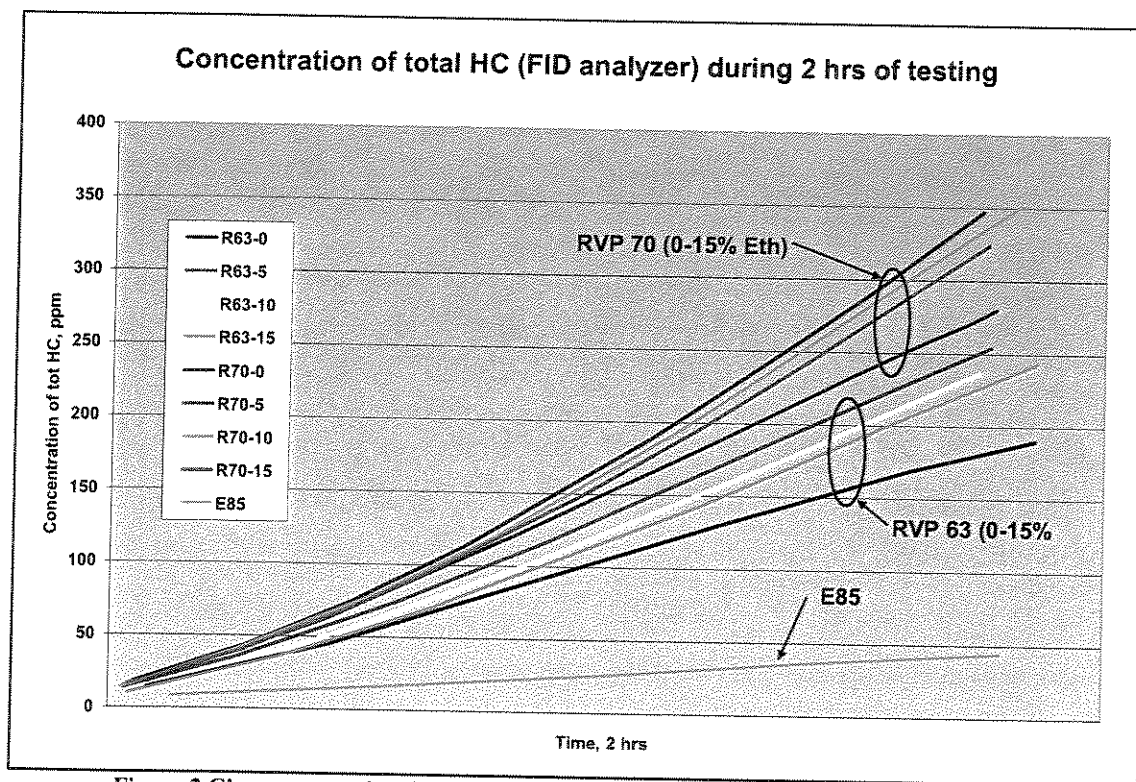


Figure 2 Changes over time in Total Hydrocarbon Concentration (FID) in the VT Shed

## 4.2 Changes over time for other components (MS).

### 4.2.1 Ethanol

Unsurprisingly, the ethanol content of the vapour proved to increase with increasing ethanol content in the test container to some extent. However, the relationship was not linear. Two factors contribute to this pattern. Naturally, the vapour pressure is positively correlated to the ethanol content of the blend in the container. In addition, however, ethanol enhances the vapour pressure according to a relationship that is not linear and peaks at relatively low ethanol contents of around 10% in ethanol-gasoline blends. This is shown here since the vapour contents (ppm) were virtually the same for both the 5% and 10% blends, while those of both the 0% and the E85 blends were considerably lower.

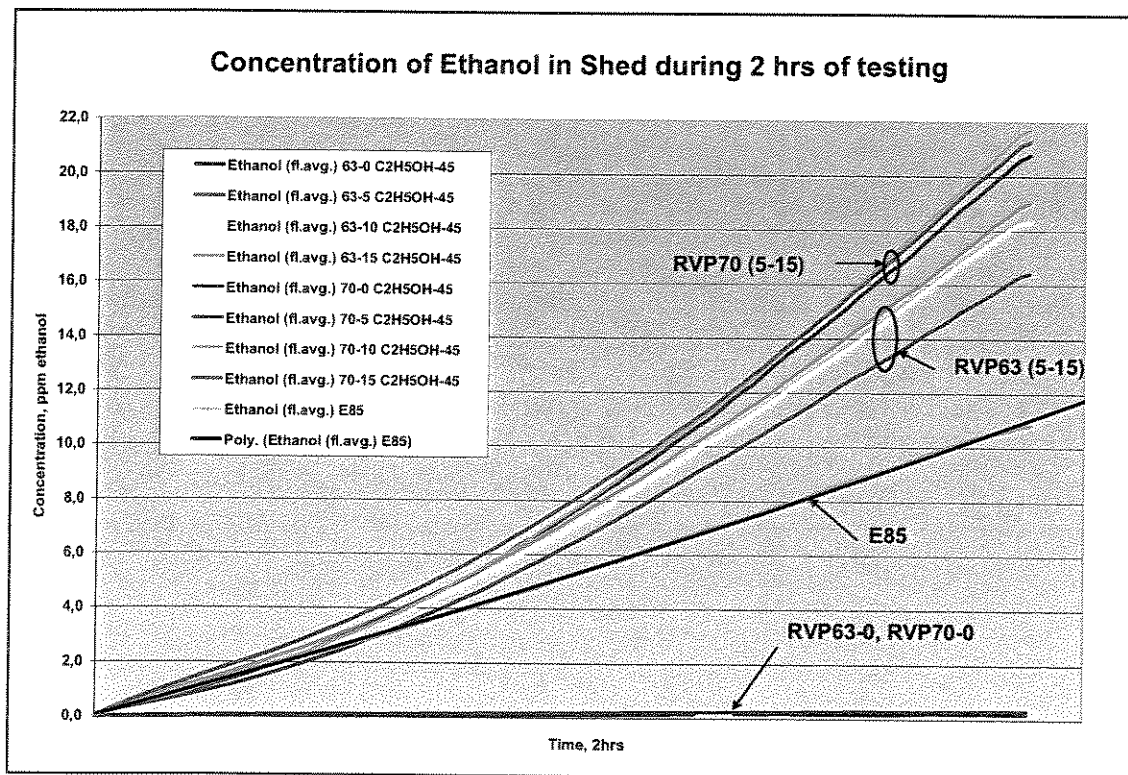


Figure 3 Changes over time in the Ethanol Concentration in the VT Shed

## 4.2.2 Butane

Butane is the main compound used to regulate the vapour pressure of gasoline. It is removed to reduce the vapour pressure when required, for instance in summer gasoline, which is used in higher ambient temperature ranges. The gasoline with the higher Reid Vapour Pressure (RVP) index was therefore expected to have a higher content of vaporizing butane. This expectation was confirmed in the tests, as shown below. In addition, the butane vapour pressure-enhancing effect of the ethanol blended in the base gasolines was probably maximal at contents between 5 and 10%.

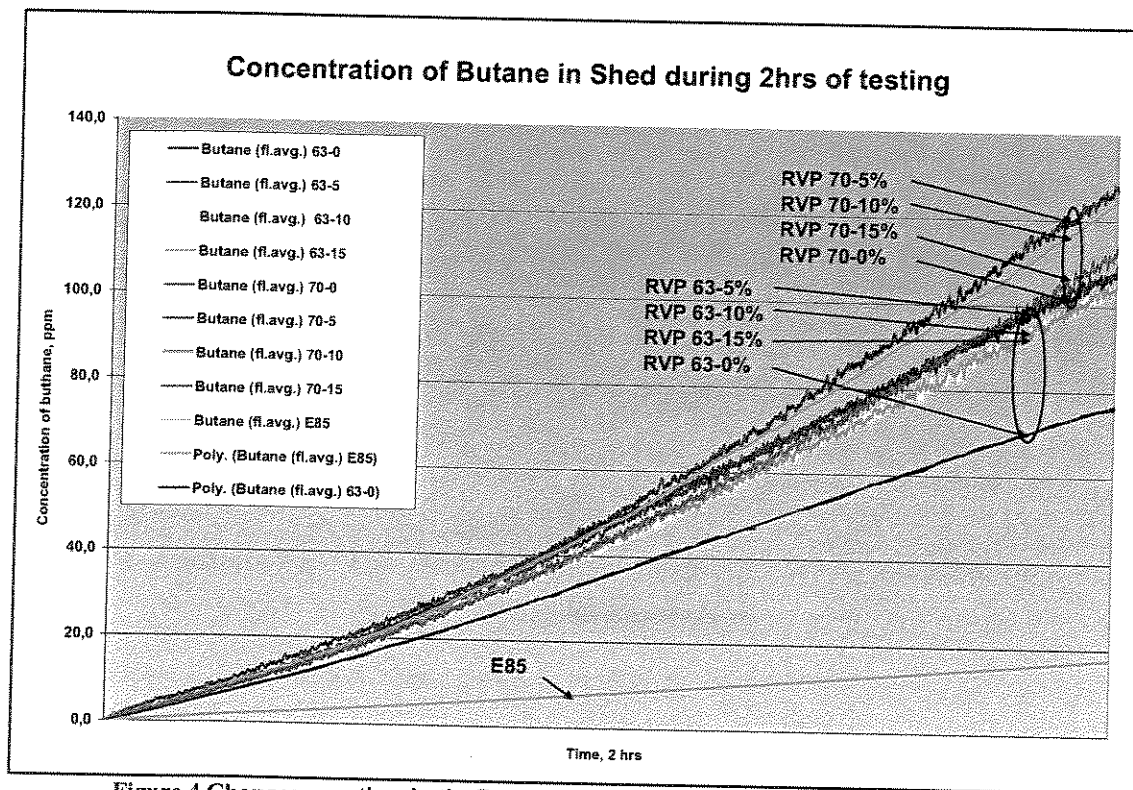


Figure 4 Changes over time in the Butane Concentration in the VT Shed

## 4.2.3 Benzene

Benzene is an aromatic hydrocarbon with both ozone formation and carcinogenic potential, so its emission levels are strictly restricted. Aromatics, however, are widely used to substitute lead as an anti-knock compound in gasoline.

Benzene is also created during the combustion process in engines.

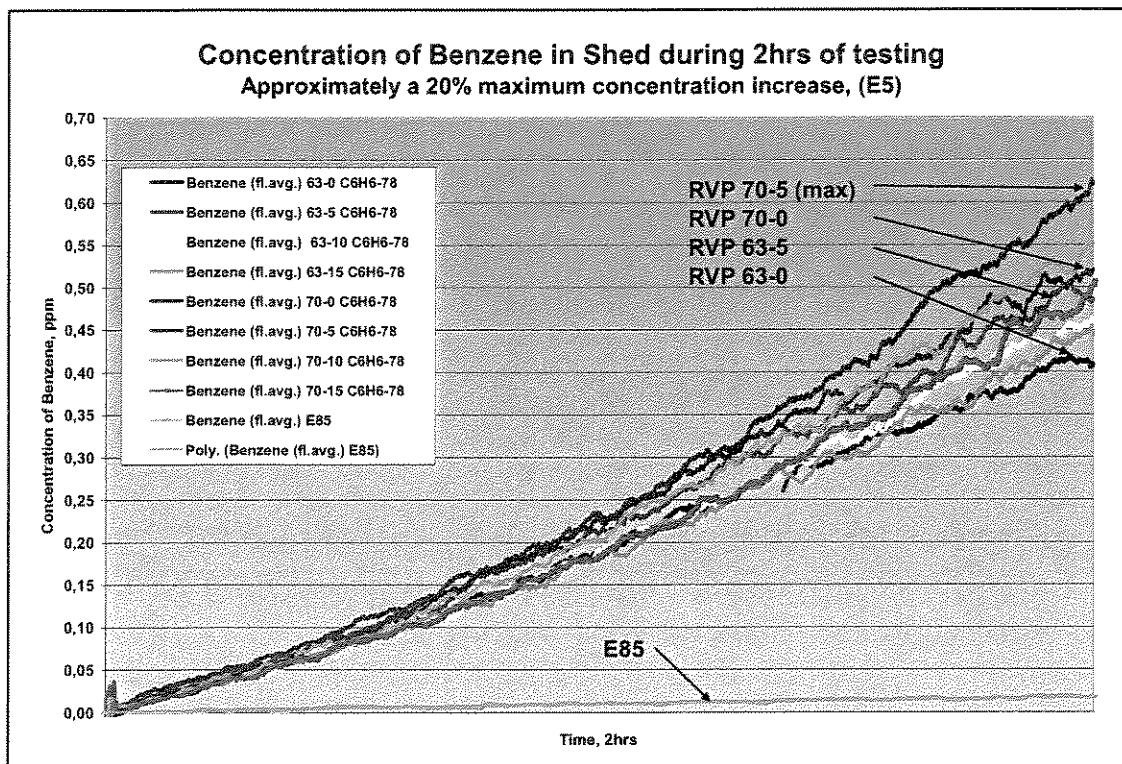


Figure 5 Changes over Time in the Benzene Concentration in the VT Shed

Max concentration increase compared to base levels: approx. 20% (with E5)'.



### 4.2.4 Toluene and Xylene

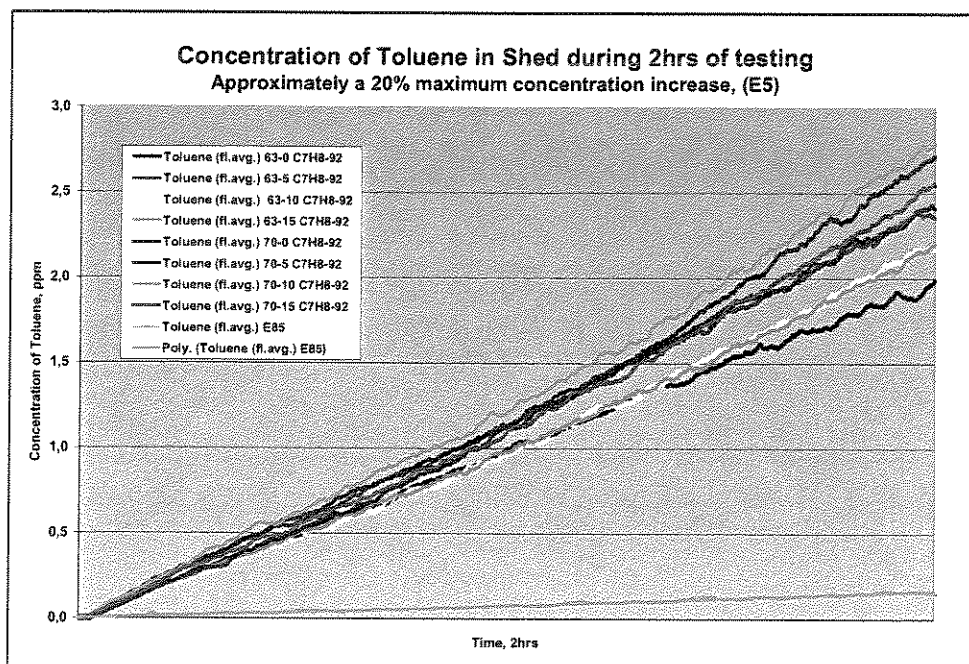


Figure 6 Changes over Time in the Toluene Concentration in the VT Shed

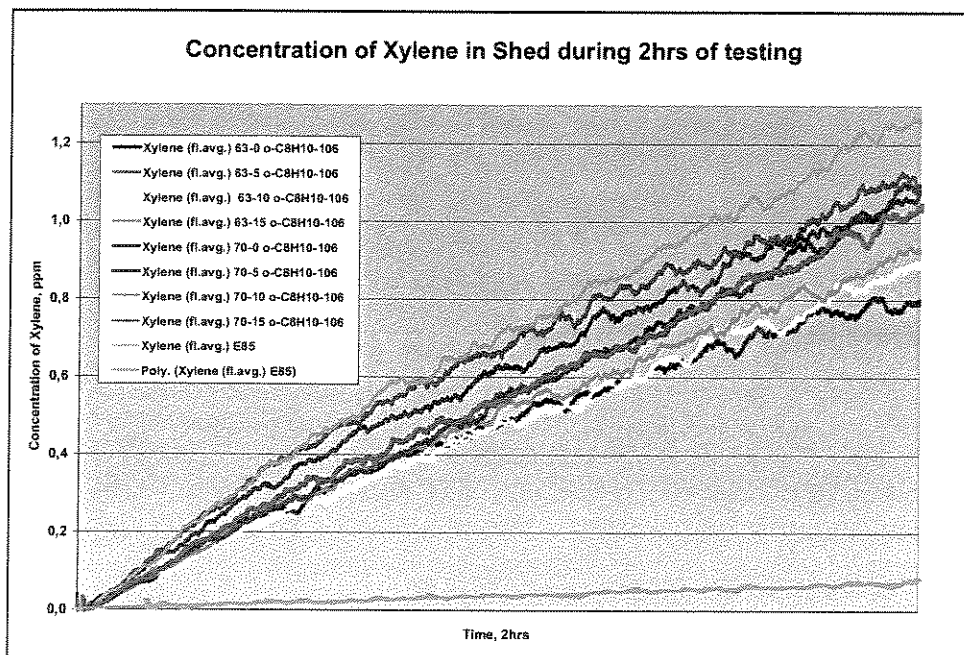
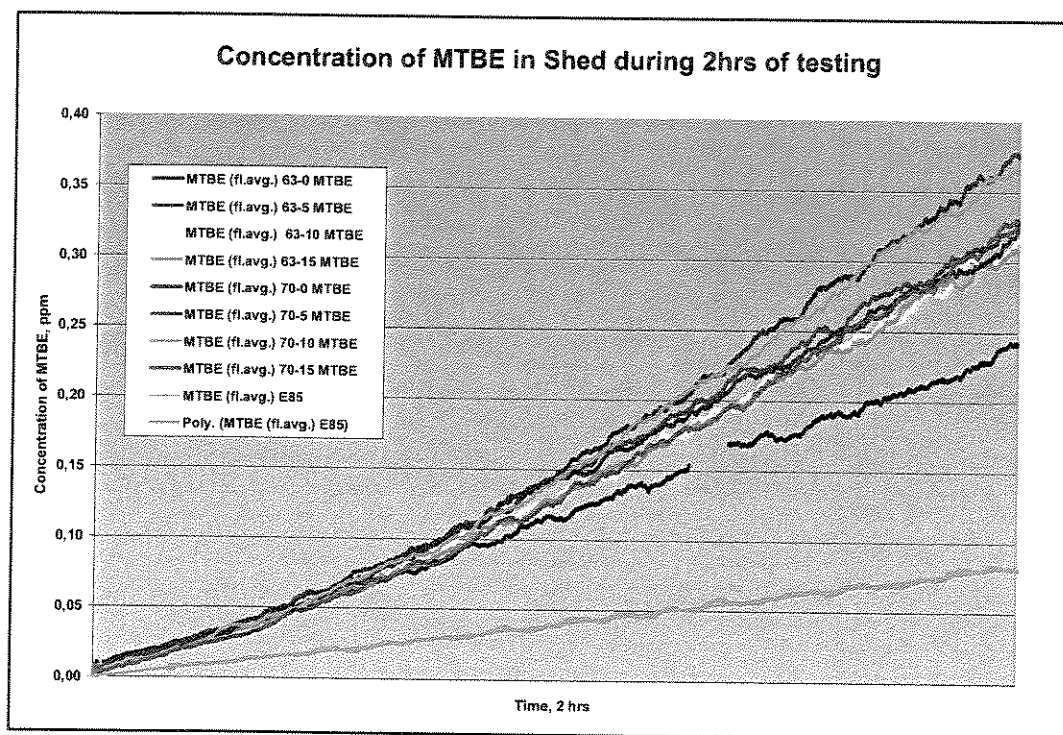


Figure 7 Changes over Time in the Xylene Concentration in the VT Shed

Max concentration increase compared to base levels: approx. 20% (with E5)



## 4.2.5 MTBE

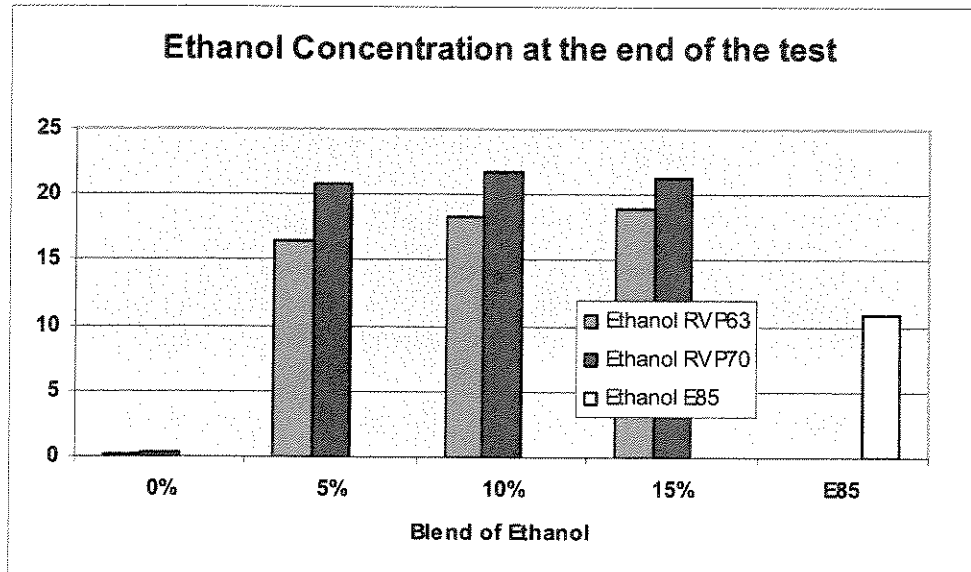


**Figure 8 Changes over Time in the MTBE Concentration in the VT Shed**

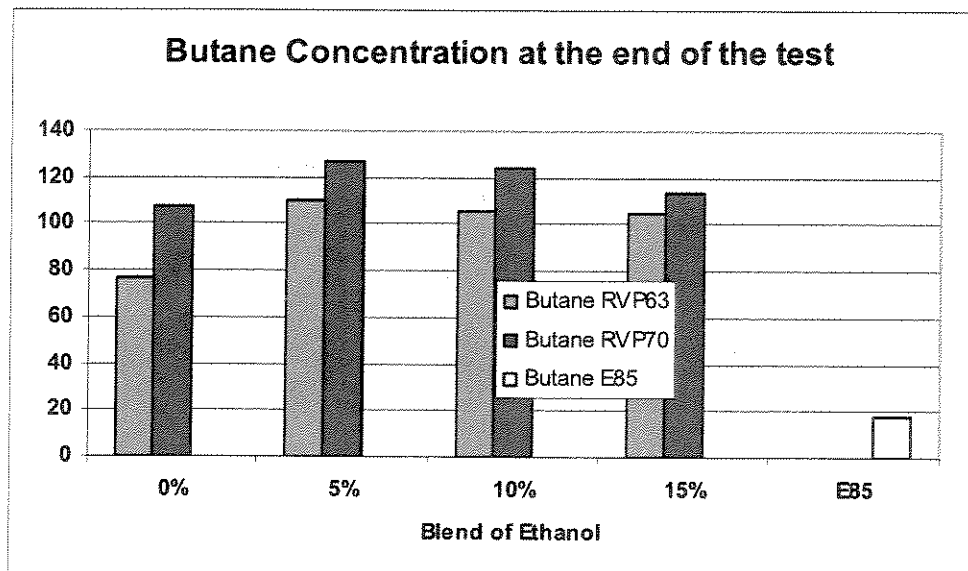
Max concentration increase compared to base levels: approx. 20% (with E5)'

## 4.3 Comparison of final values, Bar graphs

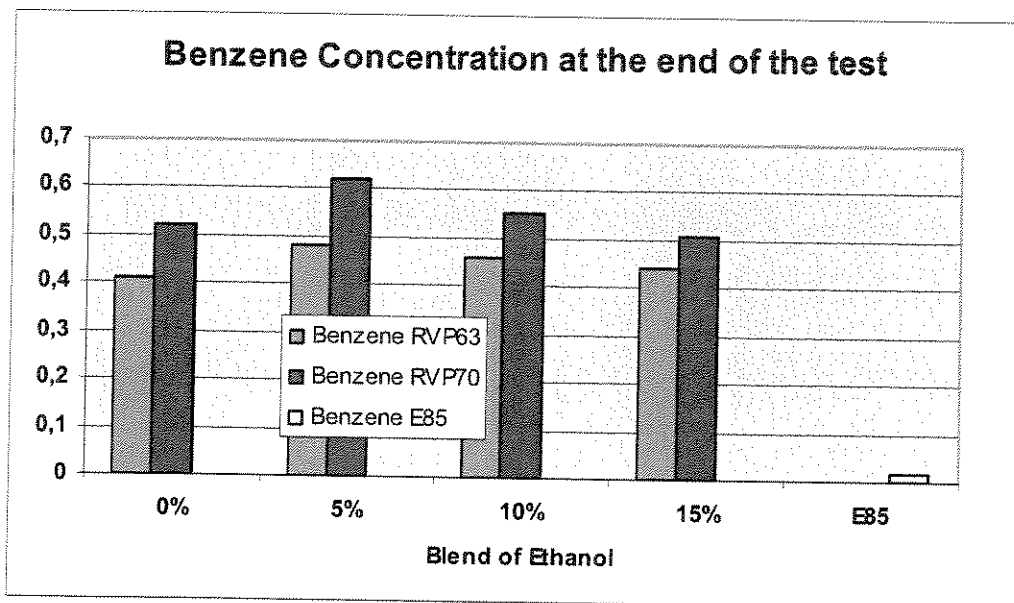
The concentrations of the measured emissions from E85 are included as a separate series since we have no information on the vapour pressure of the base gasoline used for blending. However, it probably has a relatively high RVP since this level of ethanol lowers the Reid Vapour Pressure of the final mix.



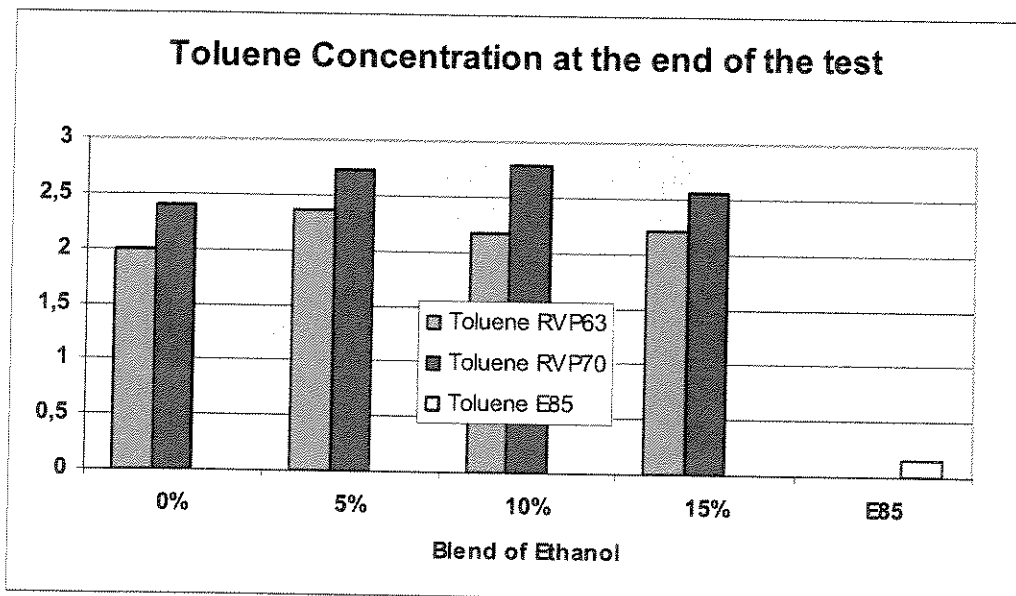
Bar graph 1. Ethanol concentration at the end of the test (ppm)



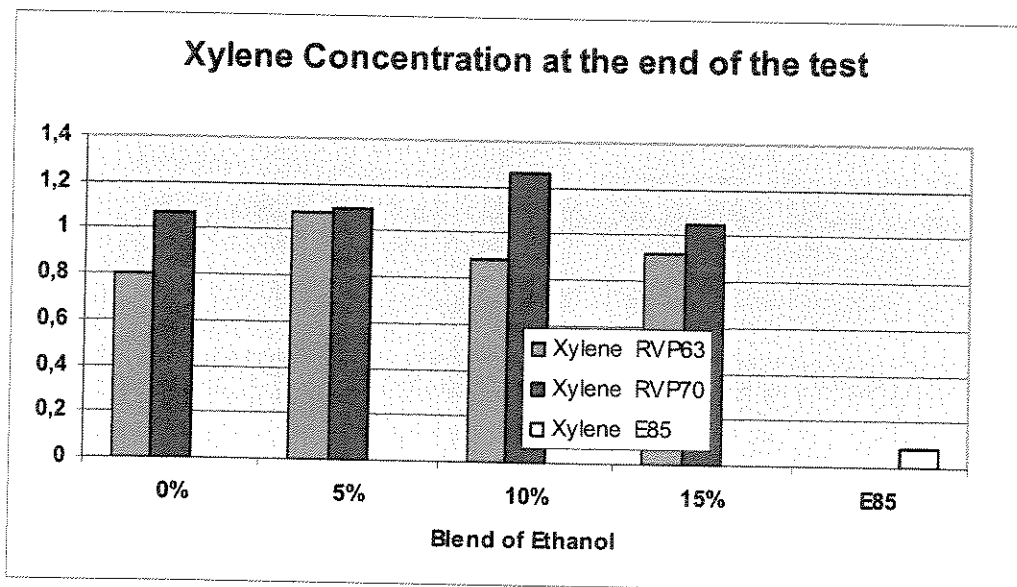
Bar graph 2. Butane concentration at the end of the test (ppm)



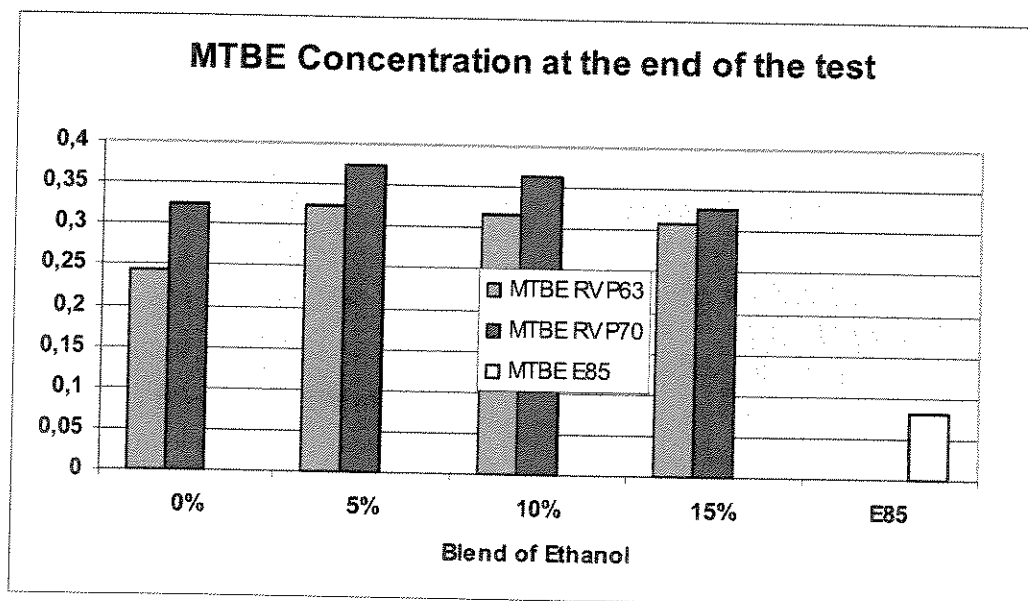
Bar graph 3. Benzene concentration at the end of the test (ppm)\*\*



Bar graph 4. Toluene concentration at the end of the test (ppm)



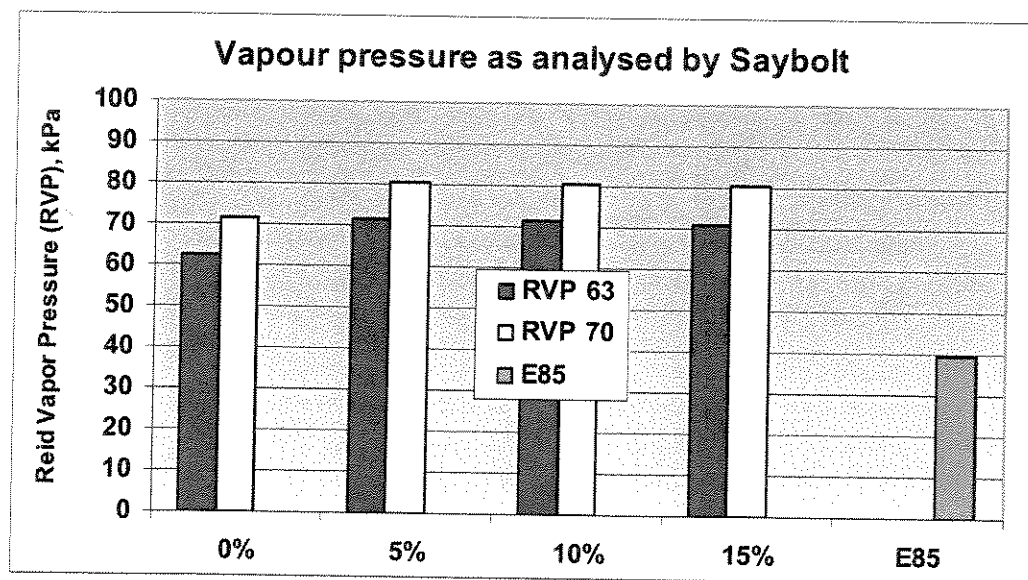
Bar graph 5. Xylene concentration at the end of the test (ppm)



Bar graph 6. MTBE concentration at the end of the test (ppm)

## 4.4 Vapour pressure analyses

A small amount of each of the gasoline and ethanol blends was sampled and sent for analysis to Saybolt Co. The results are shown in Bar graph 7. The samples were packed in gas-proof containers, provided by the company, to prevent any components escaping and thus changing the properties of the sample before analysis.



Bar graph 7. Results from the Reid Vapour Pressure analyses by Saybolt

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